

**2015-1777**

---

**IN THE  
UNITED STATES COURT OF APPEALS  
FOR THE FEDERAL CIRCUIT**

---

**E.I. DU PONT DE NEMOURS AND COMPANY**

*Plaintiff-Appellant,*

v.

**MACDERMID PRINTING SOLUTIONS, L.L.C.,**

*Defendant-Appellee.*

---

Appeal from the United States District Court for the District of New Jersey in Case No. 3:06-cv-03383, Judge Mary L. Cooper.

---

**NONCONFIDENTIAL BRIEF FOR PLAINTIFF-APPELLANT**

---

Jennifer S. Swan  
Jeffrey D. Smyth  
FINNEGAN, HENDERSON, FARABOW,  
GARRETT & DUNNER, LLP  
3300 Hillview Avenue  
Palo Alto, CA 94304-1203  
(650) 849-6600

Mary K. Ferguson  
FINNEGAN, HENDERSON, FARABOW,  
GARRETT & DUNNER, LLP  
Two Seaport Lane  
Boston, MA 02210-2001  
(617) 646-1600

Charles E. Lipsey  
FINNEGAN, HENDERSON, FARABOW,  
GARRETT & DUNNER, LLP  
Two Freedom Square  
11955 Freedom Drive  
Reston, VA 20190-5675  
(571) 203-2700

Howard W. Levine  
Aaron Gleaton Clay  
FINNEGAN, HENDERSON, FARABOW,  
GARRETT & DUNNER, LLP  
901 New York Avenue, NW  
Washington, DC 20001-4413  
(202) 408-4000

Charles D. Ossola  
Matthew J. Ricciardi  
VINSON & ELKINS LLP  
2200 Pennsylvania Avenue NW  
Washington, DC 20037-1701  
(202) 639-6500

*Attorneys for Plaintiff-Appellant*

September 18, 2015

**Certificate of Interest**

Counsel for Appellant E.I. du Pont de Nemours and Company certifies the following:

The full name of every party or amicus represented by me is:

E.I. du Pont de Nemours and Company

The name of the real party in interest (if the party named in the caption is not the real party in interest) represented by me is:

N/A

All parent corporations and any publicly held companies that own 10 percent or more of the stock of the party or amicus curiae represented by me are:

DuPont has no parent corporation, and there is no publicly-held corporation that owns 10% or more of its stock.

The names of all law firms and the partners or associates that appeared for the party or amicus now represented by me in the trial court or agency or are expected to appear in this court are:

FINNEGAN, HENDERSON, FARABOW, GARRETT & DUNNER, LLP

Charles E. Lipsey

Howard W. Levine

Jennifer S. Swan

Mary K. Ferguson

Aaron Gleaton Clay (f/k/a Aaron Vernard Gleaton)

Jeffrey D. Smyth

MCCARTER & ENGLISH, LLP

John E. Flaherty

Amit R. Parikh

Ravin R. Patel

William J. O'Shaughnessy

Michael P. Kelly

**CONNELL FOLEY, LLP**

Richard D. Catenacci  
Jennifer C. Critchley  
Tricia B. O'Reilly

**VINSON & ELKINS LLP**

Charles D. Ossola  
Matthew J. Ricciardi

**COZEN O'CONNOR**

Maria J.C. Heard

**MORGAN & FINNEGAN, LLP**

John T. Gallagher

**BARTLIT BECK HERMAN PALENCHAR & SCOTT LLP**

Lindley J. Brenza

John S. Phillips

Adam L. Hoeflich

Andre M. Pauka

**DICKSTEIN SHAPIRO LLP**

Dawn Rudenko Albert (f/k/a Dawn Rudenko)

Dipu A. Doshi

Dionne C. Lomax – Mintz, Levin, Cohn, Ferris, Glovsky & Popeo PC (formerly Vinson & Elkins LLP)

Andrew J. Allen - Budd Larner PC (formerly Vinson & Elkins LLP and Dickstein Shapiro LLP)

Andrew Phillips - Caterpillar Inc. (formerly Dickstein Shapiro LLP)

Daniel P. Archibald - United Technologies (formerly Dickstein Shapiro LLP)

Milton A. Marquis – Cozen O'Connor (formerly Dickstein Shapiro LLP)

## **TABLE OF CONTENTS**

TABLE OF AUTHORITIES .....	iv
TABLE OF ABBREVIATIONS .....	viii
STATEMENT OF RELATED CASES .....	ix
JURISDICTIONAL STATEMENT .....	x
I. STATEMENT OF THE ISSUES .....	1
II. PRELIMINARY STATEMENT .....	2
III. STATEMENT OF THE CASE .....	5
A. The Parties and the Dispute.....	5
B. Nature and Stage of the Proceedings .....	6
IV. STATEMENT OF FACTS .....	8
A. Introduction to Flexographic Printing .....	8
1. Analog Imaging.....	8
2. Solvent Development.....	11
3. Thermal Development .....	12
4. Digital Imaging .....	14
B. DuPont's Invention Claimed in the '859 Patent Resulted in a Commercially Successful Digital Thermal Process with Unexpectedly Superior Image Quality .....	19
C. The Claimed Invention of the '758 Patent .....	22
D. The District Court's Opinion.....	24
V. SUMMARY OF ARGUMENT.....	27
VI. ARGUMENT .....	30

A.	Standard of Review .....	30
B.	Disputed Factual Issues Preclude Summary Judgment of Obviousness.....	31
1.	There Are Genuine Issues of Material Fact Concerning Whether One Skilled in the Art Would Have Been Motivated to Use Thermal Methods to Develop a Digitally-Imaged Plate.....	32
2.	The District Court's Flawed Analysis Fell Prey to Hindsight by Failing to Properly Consider Objective Evidence of Nonobviousness En Route to its Obviousness Decision.....	40
3.	The Flexible Obviousness Standard of <i>KSR</i> Does Not Sanction Invasion of the Province of the Jury to Draw Reasonable Inferences From the Evidence.....	45
C.	Summary Judgment of Noninfringement of the '758 Patent Should Be Reversed .....	46
1.	Standard of Review.....	46
2.	The District Court's Claim Construction of the Term "Dimensionally Stable" Violated This Court's Precedent .....	47
a.	The District Court Improperly Limited the Claims by Reading in Limitations from the Specification .....	47
b.	There Was No Clear Disavowal of Literal Claim Scope.....	49
c.	MacDermid Led the District Court Into Error.....	53
d.	The District Court Further Improperly Limited the Annealing Process .....	55
3.	The District Court Improperly Resolved Disputed Factual Issues In Evaluating the Accused Products .....	56

VII. CONCLUSION.....59

**CONFIDENTIAL MATERIAL OMITTED**

The material omitted on pages 5, 6, 18, 22, 39, 41, and 42 concerns information from Appellee's internal memoranda, which the Appellee designated as confidential before the district court and which were filed under seal.

**TABLE OF AUTHORITIES**

	<b>Page(s)</b>
<b>FEDERAL CASES</b>	
<i>AFG Indus., Inc. v. Cardinal IG Co.,</i> 375 F.3d 1367 (Fed. Cir. 2004) .....	51
<i>Allen Archery, Inc. v. Browning Mfg. Co.,</i> 819 F.2d 1087 (Fed. Cir. 1987) .....	44
<i>Anderson v. Liberty Lobby, Inc.,</i> 477 U.S. 242 (1986).....	30, 31, 36, 45
<i>AstraZeneca LP v. Breath Ltd.,</i> 542 F. App'x 971 (Fed. Cir. 2013) .....	51, 52
<i>In re Baird,</i> 16 F.3d 380 (Fed. Cir. 1994) .....	34
<i>Baldwin Graphic Sys., Inc. v. Siebert, Inc.,</i> 512 F.3d 1338 (Fed. Cir. 2008) .....	51
<i>In re Best,</i> 562 F.2d 1252 (C.C.P.A. 1977) .....	54
<i>Cardiac Pacemakers, Inc. v. St. Jude Med., Inc.,</i> 381 F.3d 1371 (Fed. Cir. 2004) .....	35
<i>Crocs, Inc. v. Int'l Trade Comm'n,</i> 598 F.3d 1294 (Fed. Cir. 2010) .....	32, 43
<i>In re Cyclobenzaprine Hydrochloride Extended-Release Capsule Patent Litig.,</i> 676 F.3d 1063 (Fed. Cir. 2012) .....	<i>passim</i>
<i>E.I. du Pont de Nemours &amp; Co. v. MacDermid, Inc.,</i> No. 06-3383, 2008 WL 4952450 (D.N.J. Nov. 19, 2008).....	7
<i>E.I. du Pont de Nemours &amp; Co. v. MacDermid Printing Solutions, L.L.C.,</i> 525 F.3d 1353 (Fed. Cir. 2008) .....	6, 7

<i>Ecolochem, Inc. v. S. Cal. Edison Co.</i> , 227 F.3d 1361 (Fed. Cir. 2000) .....	42
<i>Frolow v. Wilson Sporting Goods Co.</i> , 710 F.3d 1303 (Fed. Cir. 2013) .....	30, 31, 36, 58
<i>Gen. Elec. Co. v. Nintendo Co.</i> , 179 F.3d 1350 (Fed. Cir. 1999) .....	31
<i>Genetics Inst., LLC v. Novartis Vaccines &amp; Diagnostics, Inc.</i> , 655 F.3d 1291 (Fed. Cir. 2011) .....	32
<i>Graham v. John Deere Co. of Kansas City</i> , 383 U.S. 1 (1966).....	31, 41
<i>Howmedica Osteonics Corp. v. Wright Med. Tech., Inc.</i> , 540 F.3d 1337 (Fed. Cir. 2008) .....	50
<i>Insite Vision Inc. v. Sandoz, Inc.</i> , 783 F.3d 853 (Fed. Cir. 2015) .....	35
<i>Invitrogen Corp. v. Clontech Labs. Inc.</i> , 429 F.3d 1052 (Fed. Cir. 2005) .....	53
<i>Ivera Med. Corp. v. Hospira Inc.</i> , No. 14-1613, 14-1614, 2015 WL 5214621 (Fed. Cir. Sept. 8, 2015) .....	31
<i>J.T. Eaton &amp; Co. v. Atl. Paste &amp; Glue Co.</i> , 106 F.3d 1563 (Fed. Cir. 1997) .....	42
<i>KSR International Co. v. Teleflex Inc.</i> , 550 U.S. 398 (2007).....	<i>passim</i>
<i>Leo Pharm. Prods., Ltd. v. Rea</i> , 726 F.3d 1346 (Fed. Cir. 2013) .....	32, 39, 40, 41
<i>Liebel-Flarsheim Co. v. Medrad, Inc.</i> , 358 F.3d 898 (Fed. Cir. 2004) .....	50
<i>Lindemann Maschinenfabrik GMBH v. Am. Hoist &amp; Derrick Co.</i> , 730 F.2d 1452 (Fed. Cir. 1984) .....	43

<i>Markman v. Westview Instruments, Inc.,</i> 517 U.S. 370 (1996).....	47
<i>Microsoft Corp. v. i4i Ltd. P'ship,</i> 131 S. Ct. 2238 (2011).....	30
<i>Mintz v. Dietz &amp; Watson, Inc.,</i> 679 F.3d 1372 (Fed. Cir. 2012) .....	37, 41
<i>Monarch Knitting Mach. Corp. v. Sulzer Morat Gmbh,</i> 139 F.3d 877 (Fed. Cir. 1998) .....	45
<i>Nat'l Steel Car, Ltd. v. Canadian Pac. Ry., Ltd.,</i> 357 F.3d 1319 (Fed. Cir. 2004) .....	34
<i>Omega Eng'g, Inc. v. Raytek Corp.,</i> 334 F.3d 1314 (Fed. Cir. 2003) .....	50
<i>Otsuka Pharm. Co. v. Sandoz, Inc.,</i> 678 F.3d 1280 (Fed. Cir. 2012) .....	32
<i>Phillips v. AWH Corp.,</i> 415 F.3d 1303 (Fed. Cir. 2005) (en banc) .....	49, 50
<i>Plantronics, Inc. v. Aliph, Inc.,</i> 724 F.3d 1343 (Fed. Cir. 2013) .....	<i>passim</i>
<i>Power-One, Inc. v. Artesyn Techs., Inc.,</i> 599 F.3d 1343 (Fed. Cir. 2010) .....	44
<i>Rockwell Int'l Corp. v. United States,</i> 147 F.3d 1358 (Fed. Cir. 1998) .....	34
<i>Ruiz v. A.B. Chance Co.,</i> 234 F.3d 654 (Fed. Cir. 2000) .....	34
<i>Shire Dev., LLC v. Watson Pharm., Inc.,</i> 787 F.3d 1359 (Fed. Cir. 2015) .....	50
<i>Stratoflex, Inc. v. Aeroquip Corp.,</i> 713 F.2d 1530 (Fed. Cir. 1983) .....	40

<i>Tec Air, Inc. v. Denso Mfg. Mich., Inc.</i> , 192 F.3d 1353 (Fed. Cir. 1999) .....	43
<i>Teva Pharm. USA, Inc. v. Sandoz, Inc.</i> , 135 S. Ct. 831 (2015).....	46
<i>Thorner v. Sony Computer Entm't Am. LLC</i> , 669 F.3d 1362 (Fed. Cir. 2012) .....	49, 50
<i>TriMed, Inc. v. Stryker Corp.</i> , 608 F.3d 1333 (Fed. Cir. 2010) .....	35
<i>Vanguard Products Corp. v. Parker Hannifin Corp.</i> , 234 F.3d 1370 (Fed. Cir. 2000) .....	52
<i>Vitronics Corp. v. Conceptronic, Inc.</i> , 90 F.3d 1576 (Fed. Cir. 1996) .....	49
<b>FEDERAL STATUTES</b>	
35 U.S.C. § 102(b) .....	6
35 U.S.C. § 103.....	1, 27, 30
35 U.S.C. § 282.....	30
<b>RULES</b>	
Fed. R. Civ. P. 54(b) .....	8
<b>OTHER AUTHORITIES</b>	
9B Charles Alan Wright & Arthur R. Miller, Federal Practice and Procedure § 2528 (3d ed. 2008).....	45

## **TABLE OF ABBREVIATIONS**

“the ’859 patent”	U.S. Patent No. 6,773,859
“the ’758 patent”	U.S. Patent No. 6,171,758
“PTO”	U.S. Patent and Trademark Office
“DuPont”	E.I. du Pont de Nemours and Company
“MacDermid”	MacDermid Printing Solutions, L.L.C.
A____, xx:yy	For a cite to a patent, “A____” refers to appendix page of patent, “xx” refers to column, “yy” refers to line.
A____:xx	For a cite to a transcript, “A____” refers to appendix page of transcript, “xx” refers to line.
<i>Italicized text</i>	All emphases in this brief have been added unless otherwise noted.

**STATEMENT OF RELATED CASES**

An appeal from the same civil action in the district court was previously before this Court. *See E.I. du Pont de Nemours & Co. v. MacDermid Printing Solutions, L.L.C.*, 525 F.3d 1353 (Fed. Cir. 2008) (vacating the district court's order denying a motion for preliminary injunction and remanding for further proceedings).

**JURISDICTIONAL STATEMENT**

(A) The United States District Court for the District of New Jersey had jurisdiction over this action under 28 U.S.C. § 1338(a).

(B) The statutory basis for jurisdiction of this Court is 28 U.S.C. § 1295(a)(1).

(C) Plaintiff-Appellant filed a timely Notice of Appeal on June 25, 2015.

(D) This appeal is from a final judgment under Fed. R. Civ. P. 54(b).

## I. STATEMENT OF THE ISSUES

1. Whether the district court erred in entering summary judgment that the asserted claims of the '859 patent are invalid for obviousness under 35 U.S.C. § 103 where (1) there were genuine factual disputes regarding the teachings of the prior art, the differences between the prior art and the claimed invention, and whether there was motivation for one skilled in the art to make the claimed invention, (2) the district court did not draw reasonable inferences from the evidence in favor of the non-movant, as it was legally required to do, (3) the district court employed its own view of the evidence based on hindsight and "market forces" instead of considering the disputed expert and other evidence in the record, and (4) the district court did not consider the objective evidence of nonobviousness en route to making a decision on obviousness, but merely considered whether such evidence could rebut its prior obviousness determination.

2. Whether the district court erred in granting summary judgment of noninfringement of the '758 patent where it (1) construed the term "dimensionally stable" in the product claims of the patent by failing to apply the plain language of the claim, and, instead, improperly imported certain *process* limitations from the specification into the *product* claims, (2) further narrowed those imported process limitations in a way unsupported by the intrinsic record, and (3) improperly

resolved factual disputes on summary judgment as to whether MacDermid's process met the imported process limitations.

## **II. PRELIMINARY STATEMENT**

Through this appeal, DuPont seeks only restoration of its right to present its claims for infringement of the '859 and '758 patents for appropriate resolution by a jury. The district court improperly denied DuPont that right by violating, *inter alia*, two of the cardinal principles underlying the patent law: (1) it improperly decided disputed factual questions relating to nonobviousness of the '859 patent on summary judgment by resolving inferences to be drawn from the evidence adversely to the non-movant, and (2) it read into the product claims of the '758 patent a constellation of process limitations from the specification that conflict with the plain meaning of the claim language.

The invention claimed in the '859 patent is a method of making "flexographic" printing plates that combined high-quality "digital" imaging technology with a new form of "thermal" development technology. At a high level, "analog" imaging and thermal and "solvent" development techniques for flexographic printing plates had been known since at least the 1960s. Even though the solvent development techniques were more cumbersome, they were nonetheless known to produce plates with finer image quality than that attainable with thermal development. A quantum breakthrough in image quality occurred

with the invention in 1992 of the digital imaging process. Tellingly, DuPont and the inventor of that process taught its use *exclusively* with *solvent* development techniques, consistent with a belief that the more robust solvent development was needed to produce relief images that faithfully reflected the finer image quality attainable with their new digital imaging process. Notwithstanding that thermal development techniques had been known for some thirty years at the time of the invention of digital imaging, it was not until the invention of the '859 patent seven years later in 1999 that anyone demonstrated the successful use of thermal development to produce surprisingly high-quality plates employing digital imaging. At a minimum, those facts raised a reasonable inference that persons skilled in the art believed that thermal development was not appropriate for use with digital imaging, potentially supporting a jury-finding of nonobviousness. That inference was strengthened further here by expert opinion and substantial evidence of unexpected superior results and commercial success of the invention.

In order to avoid the insidious effects of hindsight, the district court was required to carefully weigh the objective evidence of what persons of ordinary skill in the art actually *did* before and after the invention was made and assiduously decline to resolve conflicting inferences from that evidence regarding what such persons *thought* at the time, the latter being left for the jury to resolve. The district court here failed to do so. Instead, the district court improperly drew the opposite

inference of obviousness on summary judgment based on its perception of so-called “market forces.” Applying an overly simplistic view of the Supreme Court’s decision in *KSR International Co. v. Teleflex Inc.*, 550 U.S. 398 (2007), the court concluded that because digital imaging and *different* thermal methods for analog plates both existed in the art, “market forces” would have led one skilled in the art to combine the “best” imaging technique with the “best” development technique to arrive at the invention of the ’859 patent. (A035.) Yet, the prior art thermal development processes, *lacking* a “thermally-removable” imaging layer, were *not* the development process claimed in the ’859 patent, and were clearly not the “best” technique, since they yielded poorer quality plates. Moreover, whatever flexibility may be afforded by *KSR* regarding conclusions of obviousness where the prior art provided a “finite number of identified, predictable solutions,” *KSR*, 550 U.S. at 420, it did not and could not sanction invasion of the sole province of the jury to resolve disputed inferences regarding, *inter alia*, whether or not a particular technology was in the mind of persons skilled in the art a “predictable” or the “best” solution.

The district court also erred in granting summary judgment of noninfringement of the asserted *product* claims of the ’758 patent. The term “dimensionally stable” appears in those product claims as describing the *properties* of a “polymeric substrate.” In ascertaining the meaning of this term, the district

court need have looked no further than the plain language of the remainder of the claim itself, which specifically describes the allowable distortion as less than 0.03%. (A181.) Instead, at MacDermid’s urging, the district court limited the claims by reading into them *process* limitations from the specification—a “special annealing process”—effectively limiting the claims to a preferred embodiment. This analysis violated this Court’s well-established precedent, particularly where there was not an explicit disavowal of claims scope, and warrants reversal. Compounding the error, the district court again improperly resolved genuine factual disputes in determining that MacDermid’s product did not satisfy the newly created process limitations of the claim. Accordingly, even if the district court’s construction is affirmed, reversal is still warranted.

### **III. STATEMENT OF THE CASE**

#### **A. The Parties and the Dispute**

DuPont has been a leader in the development and introduction of printing products, including flexographic printing plates, based on photopolymerizable imaging materials since the 1950s. MacDermid itself characterized DuPont’s history relevant to this dispute in 2008:

[REDACTED]

[REDACTED]

MacDermid also characterized itself, [REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

[REDACTED]

#### **B. Nature and Stage of the Proceedings**

DuPont commenced this action against MacDermid in 2006 for infringement of the '859 and '758 patents, alleging that MacDermid manufactured and sold printing elements to be used, treated, processed, or developed in a manner that infringes one or more claims of DuPont's '859 patent. (A005, n.1.) DuPont further alleged that MacDermid manufactured and sold flexographic printing plates that infringed one or more claims of the '758 patent. (*Id.*) Trial by jury was demanded. (A093.)

At the outset of the case, DuPont moved for a preliminary injunction. (A103-04.) The district court denied DuPont's motion improperly concluding the patent was likely invalid under 35 U.S.C. § 102(b) based on its misperception of the effective filing date of the '859 patent. *See E.I. du Pont de Nemours & Co. v. MacDermid Printing Solutions, L.L.C.*, 525 F.3d 1353, 1362-63 (Fed. Cir. 2008).

DuPont appealed, and the district court's decision was vacated and remanded by this Court. *Id.* On remand, the parties submitted supplemental briefing, after which the district court again denied DuPont's motion for preliminary injunction, now based principally on the Supreme Court's then-recent 2007 *KSR* decision, perceiving DuPont's invention as likely obvious as a combination of old elements. *See E.I. du Pont de Nemours & Co. v. MacDermid, Inc.*, No. 06-3383, 2008 WL 4952450, at \*28-29 (D.N.J. Nov. 19, 2008).

After the district court construed the claims (A052-92), MacDermid moved for summary judgment of noninfringement and invalidity of the '859 patent. (A006; A152.) MacDermid also moved for summary judgment of noninfringement of the '758 patent based on the court's claim construction. (*Id.*) DuPont filed a motion for summary judgment of infringement by MacDermid of the '859 patent. (A006; A153.)

The district court granted MacDermid's motion for summary judgment of invalidity of the '859 patent, again relying on *KSR*, granted MacDermid's motion for summary judgment of noninfringement of the '758 patent, and denied the remaining motions as moot. (A006; A040; A050-51.) The district court's *KSR*-based obviousness finding was based principally on DuPont's U.S. Patent No. 5,262,275 to Fan ("the Fan '275 Patent") (A2421-29), said to disclose digital

imaging, and U.S. Patent No. 5,175,072 to Martens (“the Martens ’072 Patent”) (A2182-99), said to disclose thermal development. (A022-25; A028-35.)

Following the court’s summary judgment decision, DuPont moved for entry of final judgment under Federal Rule of Civil Procedure 54(b). (A001-2; A172.) The Court granted DuPont’s motion on June 9, 2015, and entered final judgment that claims 1, 6, 22, 30, 33, 36, 39, 40, 41, and 48 of the ’859 patent are invalid as obvious and that claims 1, 3, 4, 7, and 8 of the ’758 patent are not infringed. (A001-2.) DuPont timely filed its notice of appeal on June 25, 2015, and this appeal was docketed on June 29, 2015. (A176.)

#### **IV. STATEMENT OF FACTS**

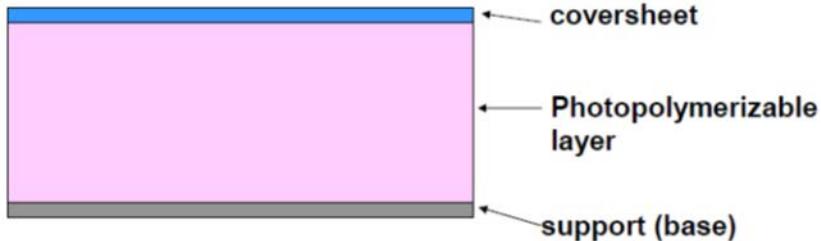
##### **A. Introduction to Flexographic Printing**

Flexographic printing plates are used to print color images on flexible labels and packaging for hundreds of everyday items, including potato chip bags, frozen vegetable bags, milk cartons, candy bar wrappers, and cereal boxes. (A184, 1:19-21; A3688-89, ¶¶ 23-24; A10715, ¶ 7.) These printing plates resemble large rubber stamps. (A3690, ¶ 25; A10715, ¶ 7.)

###### **1. Analog Imaging**

DuPont first developed flexographic printing plates with photopolymerizable materials in the 1950s. (A2965, ¶ 223.) As shown below, such plates were comprised of multiple layers, including a transparent support layer (base), an

imageable photopolymerizable layer, and a cover sheet. (A006; A3691, ¶ 28; A10715, ¶ 8.)

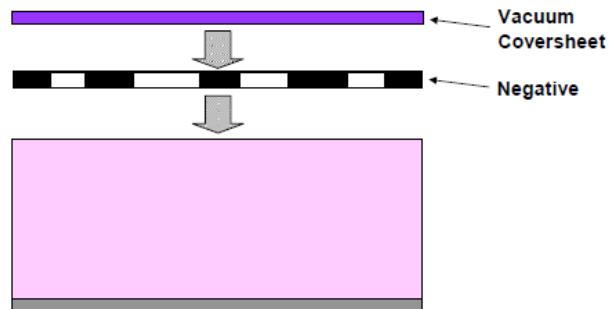


(A3692, ¶ 28.)

The photopolymerizable layer contains photoinitiators that cause a chemical reaction upon exposure to ultraviolet radiation (UV light). (A10715, ¶ 8.) This chemical reaction causes the portion of the photopolymer material exposed to the UV light to polymerize or harden. (*Id.*; A3693, ¶ 30.) The hardened, polymerized material forms the image to be printed. The remaining unpolymerized material is then removed in a development process, leaving only the hardened relief image. After development, the flexographic printing plate is mounted onto a supporting plate or roller, which is then used for printing. (A184, 1:49-50; A3690-91, ¶ 26; A3694, ¶ 32.)

Up until relatively recently, work with photopolymers in flexography used so-called “analog” imaging techniques. In analog imaging, a transparent sheet bearing a negative of the image to be printed is placed on top of the polymerizable printing plate. (A3692, ¶ 29; A184, 1:33-38.) A transparent cover sheet is placed

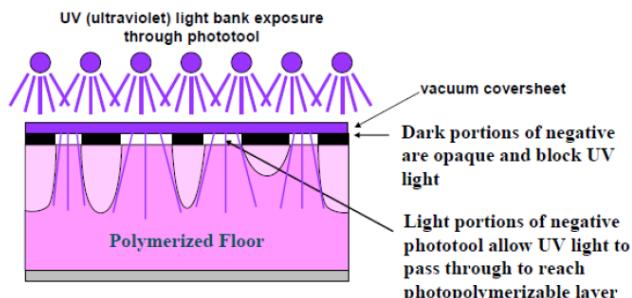
over the negative, and a vacuum is applied to secure the negative in place and to exclude air. (A3692, ¶ 29.)

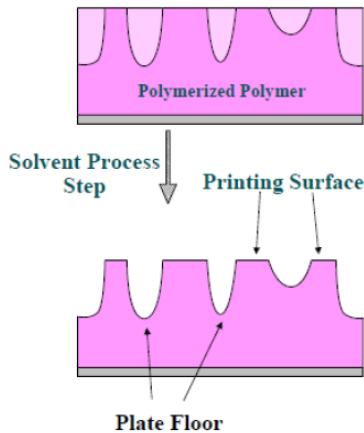


(*Id.*)

The plate is then exposed to UV light through the cover sheet and negative, whereby light enters the polymerizable layer through the transparent portions of the negative. (A3693, ¶ 30; A184, 1:38-42.) These exposed portions of the polymer layer polymerize and harden. (A3693, ¶ 30; A184, 1:42-44.)

The black or opaque areas of the negative prevent the exposure of portions of the photopolymerizable layer, whereby these portions do *not* harden or polymerize. (A3693, ¶ 30; A184, 1:44-47.) These unpolymerized portions, which are not part of the image, are then removed through a “development” process. (A3693-94, ¶¶ 30-32.) This analog imaging process is illustrated below.





(A3693, ¶ 30; A3694, ¶ 32.)

The analog imaging technique had certain inherent limitations. The fact that the photopolymer was exposed through a cover sheet and an image bearing film placed on top of the plate resulted in scattering of the UV radiation passing through the negative that limited the fineness of the relief images that could be reproduced.

(A4193-98, at A4194.)

## 2. Solvent Development

By far and away the most common technique used to develop analog plates involved a chemical solvent wash, leaving an image suitable for printing. Surface agitation and mechanical brushes were also used to help remove any remaining unpolymerized material. (A3694, ¶ 32; A184, 1:44-47.)

Solvent development was quite good for removing unexposed material and generally allowed for faithful reproduction of the super-imposed artwork within the limits imposed by the analog imaging process. The combination of analog

imaging and solvent development processes was widely used for decades.

(A10754, ¶ 12.) Nonetheless, the chemical solvents were hazardous materials that posed certain environmental risks. (A3695, ¶ 35; A10719, ¶ 16.)

### **3. Thermal Development**

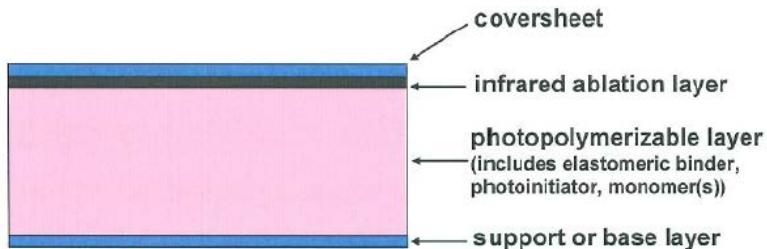
In an effort to avoid the more cumbersome aspects of solvent development of analog-imaged plates, some “thermal” development techniques had been described by DuPont and others since at least as early as the 1960s, but that technology languished. (A2938, ¶¶ 101-03; A6145.) Prior art methods of thermal development used heat to soften the unpolymerized portions of the photopolymerizable layer and then used absorbent materials, such as paper or felt, to blot away some of the liquefied unpolymerized material. (A2938-39, ¶¶ 103-106; A3108, 1:41-2:1; A3109, 4:2-5, 4:58-63.) To the extent such thermal development processes worked with analog imaging, it was because the image bearing negative was not physically attached to the underlying photopolymer layer (*see, e.g.*, A3693, ¶ 31) and did not, therefore, interfere with removal of unpolymerized portions of the photopolymer layer. The Martens '072 Patent (A2182-99), upon which the district court relied, was an example of such a dry thermal development process and was before the Examiner during prosecution of the '859 patent. (A183; A2940, ¶ 110.)

While potentially providing advantages, such as the avoidance of chemicals used for a solvent wash, thermal technology languished because of image quality problems. (A2985, ¶¶ 295-96; A3706-07, ¶¶ 59-60; A2987-89, ¶¶ 303-06; A4259-60; A4266; A6145.) The thermal technology simply did not produce high-quality images, and the quality of the printing plates produced by the combination of analog imaging and thermal development (analog thermal processes) was not comparable to the results of combinations of analog imaging with solvent development (analog solvent processes). (A3700-01, ¶¶ 47-48; A3706-07, ¶¶ 59-60; A2985, ¶ 295; A2986-89, ¶¶ 301-07; A4259-60; A4266.) As the '859 patent itself notes, "Dramatic reduction[s] in plate performance have been found as a result of thermal processing of plates." (A185, 4:4-5.) Indeed, it was not until April 1999 that the first prototype of an analog thermal process was exhibited by DuPont, and not until April 2000 (after the invention of the '859 patent), that DuPont first attempted to commercialize an analog thermal process. (A2976, ¶ 263.) The technology, however, never developed high-quality images compared to solvent processes due to the thermal method being far less effective in removing the unhardened portions of the photopolymerizable layer. (A2986-89, ¶¶ 301-07; A4259; A185, 4:4-18.) Further, the analog thermal technology failed to eliminate solvents altogether, because it still required a brief solvent wash to clean the

“floor” (the solid, fully exposed bottom) of the plate and remove remaining particles. (A2978, ¶¶ 268-269; A2967, ¶ 236.)

#### 4. Digital Imaging

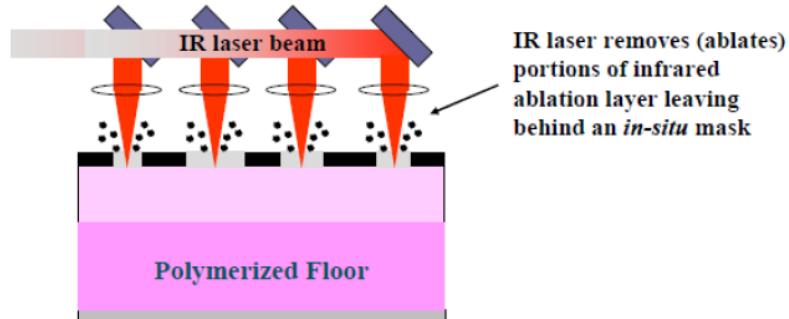
In the early-1990s, DuPont invented a new and vastly superior imaging technology to produce flexographic printing plates. (A3697-700, ¶¶ 40-44; A2966, ¶¶ 228-29; A4193-98.) This new process came to be called “digital” imaging and yielded finer image reproduction because it did not require exposure through a separate negative and cover sheet placed on top of the photopolymerizable layer. (A3697, ¶ 40; A10734, ¶ 9; A4193-98.) Instead, as shown below, the digital process used a thin, opaque “infrared ablation layer” applied directly onto the surface of the photopolymerizable layer. (A3697-700, ¶¶ 40-44; A10734, ¶ 9.)



(A3697, ¶ 40.)

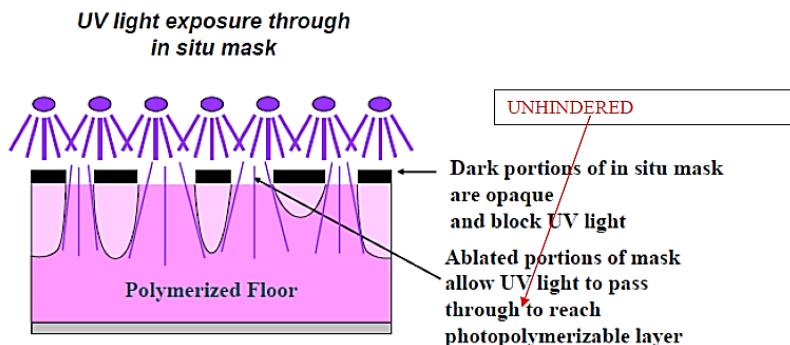
In use, the image to be printed was first digitized and stored in a computer. (A3697-98, ¶ 41.) The cover sheet was then removed, exposing the infrared ablation layer. (A3698, ¶ 42.) A computer then guided an infrared laser across the surface of the infrared ablation layer to directly remove or “ablate” select portions of the layer. (*Id.*; A10717, ¶ 12; A10734, ¶ 9.) This process created a thin, opaque

template directly on the photopolymerizable layer, forming an “in-situ mask” of the image to be printed, as shown below. (*Id.*)



(A3698, ¶ 42.)

The openings thus formed in the in-situ mask allowed UV light to pass through the mask largely unscattered, such that the portions not protected by the mask polymerized and formed an image, as shown below. (A3698-99, ¶ 43; A10718, ¶ 14; A10734, ¶ 10.)



(A3699, ¶ 43.) As with the analog plates, discussed above, a chemical solvent wash was then used to remove the unpolymerized material, leaving only the desired relief image. (A3699-700, ¶ 44.)

Digital imaging provided improved image quality over analog plates.

(A3249-52; A4188; A2836, ¶¶ 467-68; A2826-28, ¶¶ 410-14.) Improved printing properties included finer highlights, an increased tonal range, and sharp lines and dots, in part because the digital mask avoids radiation scattering and diffraction through the analog negative and in part because the photopolymerization could take place in air, rather than in the vacuum used for analog imaging. (A3249-50.)

This digital imaging method was first described in DuPont's Fan '275 Patent relied upon by the district court, which was filed on August 7, 1992 and issued on November 16, 1993. (A2421-29.) Notably, and consistent with the desire to capitalize on the higher-quality images attainable with digital imaging, the *only* development process disclosed in the Fan '275 Patent involved "washing with a suitable developer," using organic solvents or aqueous or semi-aqueous solutions, to remove the unpolymerized material. (A2426, 10:21-27; A2946, ¶ 144.) This patent was also before the Examiner during prosecution of the '859 patent. (A183; A2944, ¶ 134.)

A further improvement of the digital process by DuPont was described in a European Patent Office publication, EP 0741330, on November 24, 1999 ("the Fan '330 Publication"), which was also before the Examiner during the '859 patent prosecution. (A2009-32; A183; A2953, ¶¶ 176-77.) Like the Fan '275 Patent, the Fan '330 Publication discloses for use with digital imaging *only* a solvent

development process of “washing with a suitable developer,” using organic solvents or aqueous or semi-aqueous solutions. (A2018:11-29; A2955, ¶ 184.)

DuPont, the discoverer of digital imaging, who would reasonably be understood by those of ordinary skill in the art to be most familiar with the requirements of this new process, never described its use with thermal development processes during the seven years between the invention of digital imaging and the invention of the '859 patent in 1999, and with good reason. First, and as noted above, only the solvent development processes of the day were known to be capable of producing finer quality images with analog imaging, and the available thermal development processes were known to yield generally poor images. (A3700-01, ¶¶ 45-48; A3706-07, ¶¶ 59-60; A2985, ¶ 295; A2986-89, ¶¶ 301-07; A4259-60; A4266.) Accordingly, only the solvent development processes of the day were thought to be capable of translating the finer image quality provided by the digital imaging process into finer relief patterns in the finished plates. Second, thermal development was feasible for use with analog imaging because the image-bearing negative could be separated from the photopolymer layer prior to development and, therefore, did not interfere with melting and removal of the unexposed photopolymer. In digital imaging, however, the imaging layer was bound directly to the photopolymer layer, and could reasonably have been expected to interfere with attempts to blot away the

unexposed photopolymer beneath it—one would simply not have believed that a digital plate could be processed thermally. (A3701, ¶ 48; A2975, ¶ 260; A2976-77, ¶ 265; A2969, ¶ 241; A2971-72, ¶¶ 251-53; A2979-80, ¶¶ 274-76.)

Based on all the above, there was genuine doubt in the field as to whether thermal development could provide its claimed environmental and time saving benefits *even with analog plates*. (A2978, ¶¶ 269-70; A2976-77, ¶ 265.) The advantage of digital imaging was a sharper, clearer image, but the existing thermal development methods would have been expected to *degrade* that image. (A2984-85, ¶¶ 294-96; A2987-89, ¶¶ 305-07.) Indeed, there were questions in the art as to whether digital imaging was even compatible with the then-existing thermal methods. (A2987, ¶ 304; A2976-77, ¶ 265.) The fact that DuPont itself taught only solvent development for use with digital imaging could reasonably have been expected to impact the perceptions of persons of ordinary skill because even

MacDermid concedes that DuPont was [REDACTED]

[REDACTED] Indeed, no one actually attempted to apply thermal development technology to the new *digitally-imaged* plates until the inventors of the '859 patent did so years later.

**B. DuPont's Invention Claimed in the '859 Patent Resulted in a Commercially Successful Digital Thermal Process with Unexpectedly Superior Image Quality**

DuPont's '859 patent, entitled "Process for Making a Flexographic Printing Plate and a Photosensitive Element for Use in the Process," issued on August 10, 2004. (A183-209.) It claims, *inter alia*, methods for making flexographic printing plates using a combination of DuPont's digital imaging technology and a novel thermal development process that addressed the perceived complications arising from affixation of the laser ablative mask layer directly on the surface of the photopolymerizable layer. (*Id.*) As found by the district court, the claimed invention was "completed in the United States on or before June 9, 1999." (A022.)

In experimenting with the use of thermal development processes, DuPont noted that "[t]he portions of the additional layer[s] that remain after thermal development can alter the relief depth, reverse depth, and surface of the plate and therefore detrimentally impact printing performance of the plate." (A185, 4:14-18.) DuPont discovered that a digital imaging layer containing an infrared absorbing material, a UV absorbing material, and a binder that has a softening or melting temperature less than 190 °C, such that the viscosity of the binder will be reduced during heating, not only could form an in-situ mask that does not allow the underlying photopolymerizable layer to be unduly altered leading to a deterioration of printing quality but also could be thermally removed. (A2920-21, ¶¶ 30-32;

A188, 10:50-58; A189, 11:15-23, 11:42-12:14; A192, 17:21-43; A195, 24:3-9.)

Surprisingly, and in contrast to the poor experience with thermal development of analog-imaged plates, the thermal development of plates bearing such thermally removable digital imaging layers resulted in dramatically improved printing performance, as good as and often better than existing solvent development technologies. (A2985, ¶ 296; A3706-08, ¶¶ 59-62; A2986-89, ¶¶ 301-08.)

Contrary to the district court's improper finding on summary judgment, none of the prior art thermal development processes, including the Martens '072 Patent specifically relied on by the district court (A029), included such a thermally removable imaging layer. (A2941-43, ¶¶ 118-129.)

The claims of the '859 patent recite the process invented by DuPont that surprisingly avoided the technical barriers previously thought to prevent thermal development of digital plates. Claim 30 of the '859 patent, dependent on claim 1, is illustrative of claims directed to this new combination of digital imaging and thermal development. Reproduced in independent form, it reads:

30. A process for making a flexographic printing plate comprising:
  - 1) providing a photosensitive element comprising: *at least one photopolymerizable layer* on a support comprising an elastomeric binder, at least one monomer, and a photoinitiator, and *at least one thermally removable layer disposed above the photopolymerizable layer*, wherein the thermally removable layer is

(a) an actinic radiation opaque layer comprising (i) at least one infrared absorbing material, (ii) a radiation opaque material, wherein (i) and (ii) can be the same or different, and at least one binder having a softening or melting temperature less than 190° C.;

2) imagewise exposing the *photopolymerizable* layer to actinic radiation forming *polymerized portions and unpolymerized portions*; and

3) *thermally treating* the element of step 2) by heating to a temperature sufficient to remove the *thermally removable layer* and to remove the *unpolymerized* portions of the photopolymerizable layer and form a relief.

(A205-06, Claim 30; A2920, ¶ 29.)

DuPont commercialized this digital thermal technology as Digital Cyrel® FAST in 2001, which has been a resounding commercial success, receiving a wealth of praise from industry experts. (A2981-83, ¶¶ 281-286; A2985, ¶¶ 295-296; A2990-91, ¶¶ 310-312; A10750-57.) Between 2001 and 2006, DuPont generated more than \$90 million in sales, and its sales in the first year increased by 988%, and increased each year thereafter. (A10756-57, ¶¶ 21-22; A036-37; A2981, ¶ 282.) These sales grew at a faster rate than sales of DuPont's conventional solvent-developed plates. (A10756-57, ¶ 21.) This commercial success was due to DuPont's digital thermal process producing superior high-quality images without the costly environmental risks and delays associated with conventional solvent development.

DuPont's digital Cyrel® FAST thermal technology was awarded the Flexographic Technical Association's "Technical Innovation Award" in 2003, for its environmental impact, speed, and quality. (A2990-91, ¶ 310; A039.) The Flexographic Technical Association stated that DuPont's digital Cyrel® FAST technology "earned the recognition because the judging team made up of expert flexo[graphic] printers and prepress providers felt that the digital Cyrel® FAST technology represented a high level of technical achievement and helped users of the system achieve excellence in flexography." (A2990, ¶ 310.)

There is evidence of copying as well. Based on DuPont's digital Cyrel® FAST technology, MacDermid investigated digital thermal processes, launching its LAVA products in 2004. (A009.) In so doing, MacDermid recognized that its product was a [REDACTED]  
[REDACTED]

### **C. The Claimed Invention of the '758 Patent**

In practicing the invention of the '859 patent, it is useful to use printing plates with substrate support layers that do not significantly change size when heated. DuPont's '758 patent, entitled "Dimensionally Stable Flexographic Printing Plates," resulted from an application filed on November 8, 1994 and addresses the dimensional stability issue. (A177-82.) The specification explains that, in the prior art, the actual physical dimensions of the flexographic printing

plates were distorted when exposed to the heat necessary for thermal development. As explained by the patent, “[i]n the development of thermally developable flexographic printing plates, we have discovered that thermal distortion may become a problem, especially when precise lines, points, and images are desired by the printers who are using the plates.” (A178, 1:64-2:1.) Thus, the invention of the ’758 patent was a flexographic printing plate, whose physical “dimensions” remained “stable” in that they were not significantly distorted in the presence of heat. (A178, 1:50-2:4.) While the patent claims the dimensionally stable plates themselves, the specification further describes methods for making such dimensionally stable plates, including discussion of various “annealing” methods that can be used to make a dimensionally stable plate without significant thermal distortion. (A178, 2:47-A179, 3:40.)

Claim 1 of the ’758 patent is illustrative and recites, in relevant, part “a dimensionally stable, flexible, polymeric substrate” wherein the thermal distortion of the plate is less than 0.03% when heated:

A photosensitive plate suitable for use as a flexographic printing plate comprising a dimensionally stable, flexible, polymeric substrate and a photosensitive elastomer layer, wherein the plate has *a thermal distortion in both the machine and the transverse directions which is less than 0.03%* when the plate is exposed to actinic radiation and, after exposure, is developed at temperatures between 100 and 180° C.

(A181, Claim 1.)

Testing of some of MacDermid's printing plates established that they met these stability criteria (A5663-74, ¶¶ 16-30), and they stand accused by DuPont of infringement of the '758 patent.

#### **D. The District Court's Opinion**

On September 17, 2014, the district court issued an order simultaneously resolving several motions for summary judgment: (1) granting MacDermid's motion for summary judgment that the '859 patent was invalid for obviousness and denying MacDermid's motion for summary judgment of noninfringement as moot; (2) denying DuPont's motion for summary judgment of infringement of the '859 patent as moot; and (3) granting MacDermid's motion for summary judgment of noninfringement of the '758 patent. (A003-04; A006.)

In holding the '859 patent invalid, the district court focused on two prior art references, the Martens '072 Patent, disclosing traditional thermal development of analog-imaged plates, and the Fan '275 Patent, describing solvent development of digitally-imaged plates. (A022-25.) The district court, *on summary judgment*, specifically found that the Fan '275 Patent describes the same digital imaging of flexographic printing plates as the '859 patent, and, despite expert evidence to the contrary (*see* A2941-43, ¶¶ 118-29), that the Martens '072 Patent describes "the same process of thermal development" as the '859 patent. (A028-29.) The district court apparently reached this finding by performing its own comparison of the text

of the two patents. (A029.) Based on these findings, the district court then focused on whether it would be obvious to combine the Fan '275 Patent and Martens '072 Patent to reach the claimed invention. (A029-30.)

In so doing, the court considered MacDermid's assertions concerning market forces (i.e., "known design incentives"), the allegedly finite number of options (only a few known techniques) for development, and the benefits of thermal development (less expensive/fewer environmental issues). (A029-35.) In response, DuPont pointed out that none of the prior art "digital solvent" references suggested using thermal development techniques, pointed out that there was no reason for one of skill in the art to believe the prior thermal techniques would work for digital development, and presented expert evidence demonstrating the difference between the thermal processes of the prior art and that recited in the '859 patent claims. (A030; A2940-43, ¶¶ 110-129; *see generally* A2907-91; A3676-708.) In improperly resolving these factual disputes on summary judgment, the district court credited MacDermid's evidence, improperly drawing inferences in *MacDermid's favor*, and discounted DuPont's evidence, apparently ignoring all of DuPont's expert evidence concerning the differences in the process, including the absence from Martens of a thermally removable imaging layer. (A035; A2941-43, ¶¶ 118-29.) The district court thus found that DuPont's process for developing digital plates using a new thermal method that was recited in the

claims of the '859 patent was merely a combination of the '275 and '072 patents, and citing *KSR*, found that the invention would be obvious. (A035.)

After finding the combination obvious, the district court then addressed “secondary considerations.” (A036.) DuPont had presented evidence showing commercial success of DuPont’s products embodying the digital thermal technology, a long-felt but unmet need for a successful digital thermal process, industry praise and awards, and copying by MacDermid. (A036-39; A7401-05; A10753-58; A7561-71; A2981-91, ¶¶ 281-314.) The district court held that this evidence was not sufficient to overcome its previously reached obviousness conclusion. (A036-40.)

The district court next turned to MacDermid’s motion for summary judgment of noninfringement of the '758 patent. The dispute turned on whether the accused MacDermid product literally infringes the *product* claims of the '758 patent in view of the district court’s construction of the term “dimensionally stable.” (A040-41.) Notwithstanding that the '758 patent claim itself defines the required degree of thermal stability (thermal distortion of less than 0.03% at temperatures between 100 and 180 °C), the district court improperly construed “dimensionally stable” as requiring the claimed plates to have undergone a “special annealing process” to confer dimensional stability, and requiring that the process be separate from other manufacturing processes, including a “bonding process.”

(A091.) In essence, the district court converted the asserted *product* claims into *process* claims by reading in process limitations from the specification.

Following the district court's claim construction, DuPont's expert *still* determined that all of the claim limitations were met by an adhesive drying step conducted by MacDermid's supplier. (A049; A5673-74, ¶ 30; *see generally* A5656-708.) The expert pointed out that the drying step is performed before the substrate material is shipped to MacDermid and laminated with the photosensitive layer, and is thus not part of the "bonding process." (A049; A5663-64, ¶¶ 14-16.) The district court, however, again dismissed DuPont's evidence on summary judgment. (A049-50.) The district court found that the adhesive drying step *was* part of the bonding process and thus did not fall within the scope of the claims of the '758 patent as narrowly construed. Because an element was missing from the claim under the court's construction, the district court entered summary judgment of noninfringement. (A050-51.)

## **V. SUMMARY OF ARGUMENT**

As developed in more detail below, this Court should reverse the district court's summary judgment that the invention of the '859 patent would have been obvious under 35 U.S.C. § 103 for the following reasons.

- There were disputed issues of material fact as to the teaching of the prior art, including whether the thermal process claimed in the '859

patent was “the same” as that existing in the prior art, the differences between the prior art and the claims of the ’859 patent, and whether there was motivation for one skilled in the art to make the claimed invention—specifically whether there was motivation to employ digital imaging to obtain a high-quality image and then degrade that image using the existing inferior thermal development technology described by the prior art.

- The district court did not view the evidence in a light most favorable to DuPont as it was required to do and failed to draw all reasonable inferences in DuPont’s (the non-movant’s) favor, including the reasonable inference of nonobviousness to be drawn from the long delay between the discovery of digital imaging and any attempt to develop those images thermally.
- The district court employed its own view of the evidence based on hindsight and “market forces” instead of considering the disputed expert and other evidence in the record.
- The district court did not consider the evidence of secondary considerations en route to making a decision on obviousness, but merely considered whether such evidence could rebut the determination it had already made that “the combination of the two

technologies would be obvious to one of ordinary skill in the art.”

(A035.)

Further, this Court should reverse the district court’s summary judgment that

MacDermid does not infringe the ’758 patent for the following reasons.

- The district court failed to provide the term “dimensionally stable” in the asserted *product* claims its plain meaning as understood by those skilled in the art in light of the language in the claim and the specification—specifically that the “dimensions” of the polymeric substrate remain “stable” within the distortion limits set forth in the claim when exposed to heat.
- The district court improperly imported “a special annealing *process*” limitation from the specification into the *product* claims of the ’758 patent.
- The district court further narrowed even these improperly added process limitations by imposing conditions on when the annealing process must take place and that the annealing process cannot include the process of bonding the photoelastomer layer to the polymeric substrate.

- The district court improperly resolved factual issues as to whether MacDermid’s annealing process was separate from a bonding process.

## VI. ARGUMENT

### A. Standard of Review

Under the Patent Act, “[e]ach claim of a patent . . . shall be presumed valid . . . .” 35 U.S.C. § 282. For this reason, the party challenging the validity of a patent must prove invalidity by clear and convincing evidence. *Microsoft Corp. v. i4i Ltd. P’ship*, 131 S. Ct. 2238, 2246 (2011). The question of patent validity under § 103 is a conclusion of law reviewed de novo based on underlying predicate facts, which are reviewed under the standard appropriate to the finding being reviewed. See *In re Cyclobenzaprine Hydrochloride Extended-Release Capsule Patent Litig.*, 676 F.3d 1063, 1069 (Fed. Cir. 2012).

On summary judgment, the underlying material facts and inferences to be drawn therefrom must be free of genuine dispute. As stated by this Court, during the summary judgment stage, a court’s “function is not to ‘weigh the evidence and determine the truth of the matter’ but instead to determine whether there is a genuine issue for trial.” *Frolow v. Wilson Sporting Goods Co.*, 710 F.3d 1303, 1308 (Fed. Cir. 2013) (citing *Anderson v. Liberty Lobby, Inc.*, 477 U.S. 242, 255

(1986)). “It is the job of the fact-finder—not the court at summary judgment—to weigh that evidence and render a decision.” *Id.* at 1311.

Accordingly, in reviewing a summary judgment of invalidity, this Court determines “de novo whether the evidence in the record raises any genuine disputes about material facts. An evidentiary dispute is genuine if a jury could decide the issue either way, and its verdict would survive a motion for judgment as a matter of law.” *Gen. Elec. Co. v. Nintendo Co.*, 179 F.3d 1350, 1353 (Fed. Cir. 1999). In determining whether a genuine issue of material fact exists, a court must view the evidence in the light most favorable to the nonmoving party and draw all reasonable inferences in the non-movant’s—here DuPont’s—favor. *Liberty Lobby*, 477 U.S. at 255; *Frolow*, 710 F.3d at 1308; *Plantronics, Inc. v. Aliph, Inc.*, 724 F.3d 1343, 1355 (Fed. Cir. 2013). “[W]e resolve factual disputes against the movant.” *Ivera Med. Corp. v. Hospira Inc.*, No. 14-1613, 14-1614, 2015 WL 5214621, at \*5 (Fed. Cir. Sept. 8, 2015) (citation omitted).

#### **B. Disputed Factual Issues Preclude Summary Judgment of Obviousness**

In examining obviousness, courts consider (1) the scope and content of the prior art, (2) differences between the prior art and the claimed subject matter as a whole, (3) the level of skill in the art, and (4) objective evidence of nonobviousness. *Graham v. John Deere Co. of Kansas City*, 383 U.S. 1, 17-18 (1966); *KSR*, 550 U.S. at 406-07. A claimed combination may be nonobvious

where the prior art led away from a modification or the modification yielded more than predictable results. *See Crocs, Inc. v. Int'l Trade Comm'n*, 598 F.3d 1294, 1308-09 (Fed. Cir. 2010).

Further, the *prior art as a whole* must be examined as of the date of invention, which was found by the district court to be June 1999. *See Otsuka Pharm. Co. v. Sandoz, Inc.*, 678 F.3d 1280, 1295 (Fed. Cir. 2012) (“Taken as a whole, however, the prior art taught away from using OPC-4392 as a starting point for further antipsychotic research.”); *Genetics Inst., LLC v. Novartis Vaccines & Diagnostics, Inc.*, 655 F.3d 1291, 1305 (Fed. Cir. 2011) (indicating the prior art must be viewed as a whole, “including portions that would lead away from the invention in suit”) (citation omitted). Moreover, all the evidence, including any objective considerations such as commercial success and unexpected results, *must* be considered *before* the court reaches an obviousness determination as a means to guard against the impermissible use of hindsight. *Plantronics*, 724 F.3d at 1355; *Leo Pharm. Prods., Ltd. v. Rea*, 726 F.3d 1346, 1357 (Fed. Cir. 2013); *In re Cyclobenzaprine*, 676 F.3d at 1075-80.

**1. There Are Genuine Issues of Material Fact Concerning Whether One Skilled in the Art Would Have Been Motivated to Use Thermal Methods to Develop a Digitally-Imaged Plate**

The district court did not apply the above precedent. As a substitute, the district court relied on an overly simplistic reading of *KSR* that, according to the

district court, allowed it to rely almost entirely on its view of so-called “market forces.” (A034-35.) Initially, the district court incorrectly held that the thermal method described in the ’859 patent was the “*same process*” as that described in the prior art ’072 patent. (A029.) That was clearly wrong. (See A2941-43, ¶¶ 118-29.) The prior art thermal processes used a physically separate image-bearing film through which the plate was exposed that was removed before development. The ’859 patent employs a digitally ablated imaging layer applied directly to the photopolymer layer that is required by the claim to be “thermally removable.” The processes are thus not the “same.” (*Id.*) Indeed, DuPont presented detailed expert evidence explaining the differences between the two processes, including how the asserted claims of the ’859 patent require a thermally removable imaging layer that was *not* described in the prior art ’072 patent. (*Id.*)

The district court then held, citing almost entirely to sections of MacDermid’s brief, that due to “market forces,” one skilled in the art would have combined the two “best” techniques: the digital technology described by the ’275 patent, which produced high-quality images, with the thermal development processes described by the ’072 patent, which resulted in potential cost savings and benefits to the environment. (A028-29.) But this also is demonstrably wrong or at least genuinely disputed. The available thermal development processes were not the “best” in terms of the quality of the images they produced. (See § IV.A.3,

*supra*; *see, e.g.*, A2985, ¶¶ 295-96; A2987, ¶ 303; A3700-01, ¶¶ 47-48; A3706-07, ¶¶ 59-60.) At a minimum, the poor results obtained with thermal development of less refined analog images, coupled with the long delay before the combination of the more detailed digital imaging and thermal development was attempted, compelled the conclusion, or at least permitted the reasonable inference, that those skilled in the art believed the combination would have been inappropriate. At a minimum, that inference must be drawn in DuPont's favor on summary judgment.

Based on this flawed analysis, the district court held “that the combination of the two technologies would be obvious to one of ordinary skill in the art.” (A035.) This analysis, however, simply ignores all of DuPont's proffered evidence and resolves numerous factual disputes between the parties that cannot be decided on summary judgment. For example, the question of what a prior art reference teaches is a question of fact, and this disputed factual issue alone should have been enough to foreclose summary judgment. *See Nat'l Steel Car, Ltd. v. Canadian Pac. Ry.*, 357 F.3d 1319, 1335 (Fed. Cir. 2004) (holding that the “content of prior art presents an issue of fact”); *Ruiz v. A.B. Chance Co.*, 234 F.3d 654, 662-63 (Fed. Cir. 2000) (holding that inquiring into the scope and content of the prior art and unexpected results are factual); *In re Baird*, 16 F.3d 380, 382 (Fed. Cir. 1994) (“What a reference teaches is a question of fact.”) (citation omitted); *Rockwell Int'l Corp. v. United States*, 147 F.3d 1358, 1366 (Fed. Cir. 1998) (“We agree with the

trial court that assessing the prior art patents involved material factual issues genuinely in dispute, precluding summary judgment of anticipation.”).

Further, the questions of whether one skilled in the art would have been motivated to combine digital imaging with the then existing thermal development technology used with some analog exposure processes, and whether the high-quality printing plates attainable with the new digital thermal process invented by DuPont would have been expected, are also disputed questions of fact that cannot be resolved on summary judgment. *See, e.g., Insite Vision Inc. v. Sandoz, Inc.*, 783 F.3d 853, 860 (Fed. Cir. 2015) (“The presence or absence of a motivation to combine references in an obviousness determination is a pure question of fact”) (citation omitted); *Cardiac Pacemakers, Inc. v. St. Jude Med., Inc.*, 381 F.3d 1371, 1378 (Fed. Cir. 2004) (“Whether the prior art provides the suggestion or motivation or teaching to select from prior knowledge and combine it in a way that would produce the invention at issue is a question of fact.”) (citation omitted); *TriMed, Inc. v. Stryker Corp.*, 608 F.3d 1333, 1341 (Fed. Cir. 2010) (“[A] reasonable expectation of success in making the invention via a combination of prior art elements is a question of fact.”) (internal quotation marks and citation omitted).

Here, and as set forth above, the prior art thermal methods *failed* to produce a high-quality image, and no one had yet commercialized the technology for even

an analog-imaged plate. Indeed, DuPont only had a “prototype” at the time. (A2976, ¶ 263.) Thus, contrary to the district court’s finding of fact, that the prior art “thermal” method was the “best” method (A033-35), the evidence in the record suggested exactly the opposite. (A030-32; A3706-07, ¶¶ 59-60; A2985, ¶¶ 295-96; A2987-89, ¶¶ 303-06; A3706-07, ¶¶ 59-60.) There was simply no motivation to use digital imaging to obtain a high resolution image and then to *degrade* that image using the inferior prior art thermal development methods. Each of these points reflect factual disputes that simply could not be resolved on summary judgment, particularly where, as discussed above, the evidence *must* be viewed in a light most favorable to DuPont and all reasonable inferences *must* be drawn in DuPont’s favor. *Liberty Lobby*, 477 U.S. at 255; *Frolow*, 710 F.3d at 1308.

The appropriate rule of decision for this case is provided by cases like *Plantronics*, 724 F.3d 1343, where this Court *reversed* a district court’s improper grant of summary judgment. There, the district court, purporting to apply *KSR*, found that miniaturizing a prior art in-ear receiver while pairing it with a comfortable, adaptable, and stabilizing ear cushion was an unpatentable matter of *common sense*. *Id.* at 1354. This Court rejected that analysis. While *KSR* allowed “a flexible approach to the obviousness inquiry” that permits the consideration of “common sense” and “market forces” as sources of “reasons to combine or modify prior art references to achieve the patented invention,” this Court nevertheless

explained that “a district court’s conclusions with respect to obviousness *must find support in the record.*” *Id.* at 1354. This Court continued, stating that “[i]n determining that a person of skill in the art would have been motivated to combine the references at issue, the district court did *not cite any expert testimony indicating that there was a motivation to combine.*” *Id.* Accordingly, “[w]here . . . the necessary reasoning is absent, we cannot simply assume that ‘an ordinary artisan would be awakened to modify prior art in such a way as to lead to an obviousness rejection.’” *Id.* (citation omitted).

This Court reached a similar result in *Mintz v. Dietz & Watson, Inc.*, 679 F.3d 1372 (Fed. Cir. 2012), again reversing a summary judgment predicated only on “common sense.” *Id.* at 1377. This Court again explained that the “recitation of the words ‘common sense’ without any support adds nothing to the obviousness equation,” and that “without any record support showing that this knowledge would reside in the ordinarily skilled artisan, the district court overreached in its determination of obviousness.” *Id.*

That the district court here recited the words “market forces” as opposed to “common sense” is a distinction without a difference, as the district court was still required to support its decision by specifically pointing to evidence establishing the absence of any genuine factual dispute as to whether one skilled in the art would have been motivated to combine the claimed features. The district court’s failure

to do so here was particularly distressing as DuPont had submitted expert evidence demonstrating that the claimed and prior art thermal development processes were *different* and that there was *no* motivation to combine thermal development with digital imaging. (See §§ IV.A.3-4, *supra*; see generally A2937-81, ¶¶ 96-280; A3701, ¶ 48; A2975, ¶ 260; A2979-80, ¶¶ 274-76.) Instead, the district court relied on MacDermid’s *attorney’s* discussion of “market forces,” and literally “adopt[ed] the analysis set forth by MacDermid [in its brief] regarding the market forces.” (A035.) This is exactly the sort of analysis that the Court criticized in *Plantronics and Mintz* and warrants reversal, particularly on a *motion for summary judgment* where the district court is not permitted to choose one set of facts over the other.

*KSR* itself recognizes that for the combination to have been obvious, the combination must constitute a “*predictable* solution” that “leads to the *anticipated* success.” *KSR*, 550 U.S. at 421. And similarly, this Court has long held that a claimed invention would *not* have been obvious unless there was “reasonable expectation of success.” *In re Cyclobenzaprine*, 676 F.3d at 1070. Here, there was at least a genuine factual dispute as to whether the “reasonable expectation” that would have been “predicted” from combining digital imaging and then available thermal development was that the digital image would have been significantly *degraded*. (See § IV.A.4, *supra*; see, e.g., A2985, ¶¶ 295-96; A2987, ¶¶ 303-05;

A3701, ¶ 48.) In fact, this was DuPont's expectation when it began experimenting with the existing thermal technology. (A2987-89, ¶¶ 305-07.)

As noted above, thermal methods were initially published in the *1960's*. Yet, no one had successfully commercialized the technology even with analog exposure processes in the decades leading up to the invention date of the '859 patent, nor had anyone demonstrated the successful combination of thermal development with digital imaging for years after the invention of digital imaging.

*See Leo Pharm.*, 726 F.3d at 1359 (holding asserted patent nonobvious where inventors recognized and solved a problem that had not been solved for over a decade). DuPont, the inventor of digital imaging, consistently taught *only* solvent development of digitally-imaged plates. (*See* IV.A.4, *supra*; *see, e.g.*, A2946, ¶ 144.) DuPont would reasonably have been perceived by those of ordinary skill in the art as most knowledgeable regarding the limitations of the new digital technology, and the exclusive instruction to use solvent development would reasonably have dissuaded others from even trying the known, inferior thermal development techniques of the day. After all, DuPont was [REDACTED]

[REDACTED] This constellation of evidence and the reasonable inferences to be drawn from it should have precluded the award of summary judgment.

**2. The District Court’s Flawed Analysis Fell Prey to Hindsight by Failing to Properly Consider Objective Evidence of Nonobviousness En Route to its Obviousness Decision**

DuPont respectfully submits that the fairest reading of the district court’s opinion is that it did *not* consider DuPont’s proffered objective evidence of nonobviousness until *after* the court had already concluded that it would be obvious to combine digital imaging with thermal development. (A035-36.) The district court specifically held that “[b]ecause of these market forces, the finite number of options, and the benefits of both digital imaging and thermal development, the Court finds that the combination of the two technologies *would be obvious* to one of ordinary skill in the art.” (A035.) Then, and only then, did the district court consider what it identified as “secondary considerations” to determine whether such considerations could “*overcome MacDermid’s strong showing of obviousness.*” (A036; A038.) This constituted an error of law requiring reversal. Courts *must* consider *all* the evidence in the record, including assessing the objective evidence of nonobviousness, *before* reaching an obviousness determination. *Plantronics*, 724 F.3d at 1355 (“This court has consistently pronounced that all evidence pertaining to the objective indicia of nonobviousness must be considered *before* reaching an obviousness conclusion.”); *Leo Pharm.*, 726 F.3d at 1357; *In re Cyclobenzaprine*, 676 F.3d at 1076; *Stratoflex, Inc. v. Aeroquip Corp.*, 713 F.2d 1530, 1538 (Fed. Cir. 1983).

By considering the objective evidence *before* making any obviousness determination, courts will avoid the trap of impermissibly using hindsight to reconstruct the invention from the prior art by “develop[ing] a hunch that the claimed invention was obvious, and then construct[ing] a selective version of the facts that confirms that hunch.” *In re Cyclobenzaprine*, 676 F.3d at 1079 (citing *Graham*, 383 U.S. at 36). “These objective guideposts are powerful tools for courts faced with the difficult task of avoiding subconscious reliance on hindsight.” *Mintz*, 679 F.3d at 1378. The objective evidence of nonobviousness “can be the most probative evidence of nonobviousness in the record, and enables the court to avert the trap of hindsight.” *Leo Pharm.*, 726 F.3d at 1358; *Plantronics*, 726 F.3d at 1355. Here, the district court, led by MacDermid, fell head first into that trap and never recovered.

Further, aside from considering the objective evidence as an afterthought, the district court’s consideration of the objective evidence was fraught with error. Initially, the district court did not even consider the evidence in the record that DuPont’s invention unexpectedly solved the problems existing in the prior art concerning the image degradation problems caused by thermal development methods. (A2984-85, ¶¶ 294-96; A2987-89, ¶¶ 305-09.) Nor does it appear that the district court considered the evidence in the record that MacDermid copied the claimed invention [REDACTED]

[REDACTED]

[REDACTED]

The district court’s consideration of DuPont’s evidence of commercial success was also deeply flawed. As mentioned above, DuPont’s sales of its digital Cyrel® FAST, incorporating the digital thermal technology claimed in the ’859 patent, increased by 988% in 2002, and increased each year thereafter. (A036; A2981, ¶ 282; A10756-57, ¶¶ 21-22.) Between 2001 and 2006, sales of its digital Cyrel® FAST generated more *than \$90 million dollars*. (*Id.*) Drawing all inferences in DuPont’s favor, as the court was required to do, *Plantronics*, 724 F.3d at 1356, this evidence was more than sufficient to create a genuine factual dispute as to the obviousness of the claimed invention.

The district court, however, essentially dismissed this evidence, stating that DuPont did not reveal “more revealing statistics such as its profit.” (A037.) This again was legal error. Commercial success supports the nonobviousness of the claimed invention by showing the public’s desire for the invention as demonstrated by increased sales. And contrary to the district court’s emphasis on profits, while market share has some relevance to the analysis, commercial success is “usually shown by significant sales in a relevant market.” *J.T. Eaton & Co. v. Atl. Paste & Glue Co.*, 106 F.3d 1563, 1571 (Fed. Cir. 1997); *Ecolochem, Inc. v. S. Cal. Edison Co.*, 227 F.3d 1361, 1377 (Fed. Cir. 2000). Further, “sales figures alone are also

evidence of commercial success.” *Tec Air, Inc. v. Denso Mfg. Mich., Inc.*, 192 F.3d 1353, 1361 (Fed. Cir. 1999) (upholding a jury finding of commercial success based on Tec Air’s sales evidence, which showed that “millions of fans” with the patented component had been sold); *Lindemann Maschinenfabrik GMBH v. Am. Hoist & Derrick Co.*, 730 F.2d 1452, 1461 (Fed. Cir. 1984) (holding the district court erred by not crediting the commercial success of a product that generated \$20 million in sales).

The district court further stated that DuPont did not show a *nexus* between “the claimed invention and its purported commercial success.” (A038.) It is well-established, however, that a “prima facie case of nexus is made when the patentee shows both that there is commercial success, and that the product that is commercially successful *is the invention disclosed and claimed in the patent.*” *Crocs*, 598 F.3d at 1310-11. Here, the entirety of the district court’s opinion discusses how the claims cover the thermal digital technology, and there was expert evidence in the record that digital Cyrel® FAST was an embodiment of that technology. (A2981-82, ¶¶ 283-85.)

The district court’s discussion of long-felt need and industry praise are similarly deficient. DuPont presented evidence that although publications had described thermal methods since the 1960s, and although digital plates were invented in 1992, no one had successfully introduced processes for the thermal

development of digital plates until the 1999 invention date of the '859 patent. (A2986, ¶ 300.) Even though the district court's own opinion makes clear the benefits that would result from a successful digital thermal method, the court merely stated “[n]othing about DuPont's argument . . . demonstrates that there was a palpable need for digital thermal plates . . . .” (A038.) Taking all reasonable inferences in DuPont's favor on summary judgment, the district court's summary rejection of long-felt need evidence warrants reversal.

Finally, the district court did acknowledge the evidence of industry praise but found such evidence “vastly insufficient to overcome MacDermid's strong showing of obviousness.” (A039.) Initially, the district court should have considered this evidence *before* it reached its obviousness determination—a determination laden with findings of disputed fact that should never have been made on summary judgment. Further, “praise in the industry for a patented invention, and specifically praise from a competitor tends to ‘indicate that the invention was not obvious.’” *Power-One, Inc. v. Artesyn Techs., Inc.*, 599 F.3d 1343, 1352 (Fed. Cir. 2010) (quoting *Allen Archery, Inc. v. Browning Mfg. Co.*, 819 F.2d 1087, 1092 (Fed. Cir. 1987)).

### 3. The Flexible Obviousness Standard of *KSR* Does Not Sanction Invasion of the Province of the Jury to Draw Reasonable Inferences From the Evidence

On a motion for summary judgment, the district court is forbidden not only from resolving conflicts in the factual evidence but also from choosing between legitimate inferences to be drawn from the evidence. *Liberty Lobby*, 477 U.S. at 255 (“Credibility determinations, the weighing of the evidence, and the drawing of legitimate inferences from the facts are jury functions, not those of a judge, whether he is ruling on a motion for summary judgment or for a directed verdict.”); *Monarch Knitting Mach. Corp. v. Sulzer Morat Gmbh*, 139 F.3d 877, 883 (Fed. Cir. 1998) (“Given this evidence, a reasonable inference can—and on summary judgment must—be drawn in favor of the patentee . . . .”); *see also* 9B Charles Alan Wright & Arthur R. Miller, *Federal Practice and Procedure* § 2528 (3d ed. 2008) (“Even if the facts are undisputed as between the parties, the case must go to the jury if conflicting inferences may be drawn from the evidence . . . .”).

The flexible obviousness standard sanctioned in *KSR* did not alter that limitation on judicial power, which is imposed by the Seventh Amendment to the U.S. Constitution. Here, as discussed above, there is evidence that would permit the inference that people of ordinary skill were dissuaded from combining digital imaging with thermal development, *inter alia*, by the poor image quality theretofore obtained with thermal development processes, by the singular focus of

DuPont, the inventor of digital imaging, on the use of only solvent development, and by the unpredictability as to whether the process would work. (*See §§ IV.A.3-4, supra.*) That inference is supported by objective factors, such as the long delay in the development of digital thermal processes, the industry praise for such processes once developed, and the commercial success of such processes. (*See § VI.B.2, supra.*) And the inference is reinforced by expert opinion as well. Under these circumstances, the conclusion on summary judgment that the combination would nonetheless have been motivated with a reasonable expectation of success by “market forces” is actually an improper choice between inferences to be drawn from the evidence. That choice, however, was exclusively for the jury after trial on the merits, notwithstanding *KSR*.

### **C. Summary Judgment of Noninfringement of the '758 Patent Should Be Reversed**

#### **1. Standard of Review**

The Supreme Court recently decided that “when the district court reviews only evidence intrinsic to the patent (the patent claims and specifications, along with the patent’s prosecution history), the judge’s determination will amount solely to a determination of law, and the Court of Appeals will review that construction *de novo.*” *Teva Pharm. USA, Inc. v. Sandoz, Inc.*, 135 S. Ct. 831, 841 (2015). In this case, the district court relied solely on intrinsic evidence when construing the term “dimensionally stable” in the '758 patent claims. (A067-71.) Accordingly,

this Court reviews the district court’s claim construction *de novo*. Once a patent’s claim terms are construed, determining whether infringement has occurred is a question of fact. *Markman v. Westview Instruments, Inc.*, 517 U.S. 370, 384 (1996). As discussed thoroughly above, disputed questions of fact cannot be determined on summary judgment, and to the extent the district court found disputed facts adverse to DuPont on summary judgment, the decision must be reversed.

**2. The District Court’s Claim Construction of the Term “Dimensionally Stable” Violated This Court’s Precedent**

**a. The District Court Improperly Limited the Claims by Reading in Limitations from the Specification**

The ’758 patent describes “a flexographic printing plate having a very low degree of thermal distortion during development.” (A178, 1:51-53.) In particular, the specification explains that “dimensional stability” requires the selection of a base layer or polymeric substrate that will be suitable for the inventors’ purpose, i.e. providing a flexographic printing plate that has a thermal distortion *less than 0.03%* when thermally developed at temperatures between 100 and 180 °C. (A178, 2:19-36.) The language of claim 1 itself demonstrates that the term “dimensionally stable” refers to a certain thermal distortion limit (a property) and

*not* to a particular process used to make a dimensionally stable plate. (A181,

Claim 1.)

During *Markman* proceedings, DuPont asserted that the proper construction of the term was:

a polymeric substrate that results in a flexographic printing plate having thermal distortion of less than 0.03% when developed at temperatures between 100 and 180°C, or [results in] an individual polymeric substrate having less than 0.07% distortion when heated to temperatures from 110 to 180°C.

(A062.) In contrast, MacDermid proposed a bizarrely complicated construction that defined “dimensionally stable” *by a particular way the plate could be made*, thus:

A flexible polymeric substrate whose dimensional stability has been controlled through *a special annealing process*, namely an annealing process that: (1) is in addition and *subsequent to the heat treating steps* associated with manufacturing the polymeric film, (2) *is not the process of bonding the photosensitive elastomer layer to the polymeric substrate* and (3) comprises: (i) heating the substrate to a temperature above its glass transition temperature but below its melting temperature and at or greater than the temperature to which the substrate is later subjected during thermal development, (ii) at tensions of less than 200 psi, and (iii) for a time greater than the time required to bring the film to the annealing temperature, such that a specially annealed substrate has less thermally induced distortion than a non-specially annealed substrate.

(A062-63.)

The district court adopted MacDermid’s proposed construction as its own (A071), and in so doing, violated this Court’s black letter precedent concerning the

construction of claims. The words of a claim are generally given their “ordinary and customary meaning” as a person of ordinary skill in the art would understand them. *Phillips v. AWH Corp.*, 415 F.3d 1303, 1312-13 (Fed. Cir. 2005) (en banc) (citing *Vitronics Corp. v. Conceptronic, Inc.*, 90 F.3d 1576, 1582 (Fed. Cir. 1996)). Here, the plain meaning of the claim indicates that “dimensionally stable” means having the dimensional stability specified in the remaining text of the claim. (A181, Claim 1.) That the claimed product does not incorporate the process used to make it is amply demonstrated by the restriction requirement during prosecution, which recognized that the product and process claims are separate and distinct inventions. (A2262-65; A2275-78; A2284-85; A2287-88.)

**b. There Was No Clear Disavowal of Literal Claim Scope**

This Court has explained that “[t]here are *only* two exceptions to this general [plain meaning] rule: 1) when a patentee sets out a definition and acts as his own lexicographer, or 2) when the patentee disavows the full scope of a claim term either in the specification or during prosecution.” *Thorner v. Sony Computer Entm’t Am. LLC*, 669 F.3d 1362, 1365 (Fed. Cir. 2012) (citation omitted). Each of these exceptions requires a *clear and explicit* statement by the patentee:

The patentee may demonstrate intent to deviate from the ordinary and accustomed meaning of a claim term by including in the specification *expressions of manifest exclusion or restriction, representing a clear disavowal of claim scope. . . . It is likewise not enough that the only embodiments, or all of the embodiments, contain a particular*

*limitation. We do not read limitations from the specification into claims; we do not redefine words. . . . To constitute disclaimer, there must be a clear and unmistakable disclaimer. . . . It is the claims that define the metes and bounds of the patentee's invention.*

*Id.* at 1366-67 (internal citations and quotations omitted); *see also Omega Eng'g, Inc. v. Raytek Corp.*, 334 F.3d 1314, 1325 (Fed. Cir. 2003) (“[W]e have required the alleged disavowing statements to be both so clear as to show reasonable clarity and deliberateness, . . . and so unmistakable as to be unambiguous evidence of disclaimer.”) (internal citations omitted); *Shire Dev., LLC v. Watson Pharm., Inc.*, 787 F.3d 1359, 1365 (Fed. Cir. 2015) (“[W]hile the prosecution history can inform whether the inventor limited the claim scope in the course of prosecution, it often produces ambiguities created by ongoing negotiations between the inventor and the PTO. Therefore, the doctrine of prosecution disclaimer only applies to unambiguous disavowals.”) (citations omitted). Even if the specification recites only a *single* embodiment, that alone is insufficient to restrict the claim scope. *See Howmedica Osteonics Corp. v. Wright Med. Tech., Inc.*, 540 F.3d 1337, 1345 (Fed. Cir. 2008) (“We have repeatedly held that the fact that the specification describes only a single embodiment, standing alone, is insufficient to limit otherwise broad claim language.”); *Phillips*, 415 F.3d at 1323 (“[W]e have expressly rejected the contention that if a patent describes only a single embodiment, the claims of the patent must be construed as being limited to that embodiment.”) (citation omitted); *Liebel-Flarsheim Co. v. Medrad, Inc.*, 358 F.3d 898, 913 (Fed. Cir. 2004) (“[I]t is

improper to read limitations from a preferred embodiment described in the specification—even if it is the only embodiment—into the claims . . .”).

And this Court has consistently rejected claim constructions limiting the scope of a claimed product by the way it is manufactured. *See Baldwin Graphic Sys., Inc. v. Siebert, Inc.*, 512 F.3d 1338, 1344 (Fed. Cir. 2008) (“Courts must generally take care to avoid reading process limitations into an apparatus claim . . . because the process by which a product is made is irrelevant to the question of whether that product infringes a pure apparatus claim.”); *AFG Indus., Inc. v. Cardinal IG Co.*, 375 F.3d 1367, 1373 (Fed. Cir. 2004) (“[D]etermination of whether a particular structure is a ‘layer’ within the meaning of the claim is not affected by the method of creation of that structure.”).

For example, in *AstraZeneca LP v. Breath Ltd.*, 542 F. App’x 971 (Fed. Cir. 2013), this Court reversed the district court’s claim construction of the term “micronized powder composition.” Although it was undisputed that the plain meaning of the term did *not* require any form of sterilization, the district court had construed the disputed term to mean “heat sterilized finely divided dry particles.” *Id.* at 975. This Court *reversed*. Initially, this Court acknowledged that “[t]here is no dispute that the patent refers *only* to dry heat sterilization as the preferred method of achieving the claimed ‘micronized powder composition’ and criticizes, often sharply, other forms of sterilization.” *Id.* at 976. Nevertheless, the Court

stated that the defendants could not point to any statements rising to the “level of clear disavowal,” holding that “[i]t is likewise not enough that the *only* embodiments, or *all of the* embodiments, contain a particular limitation.” *Id.*

Similarly, in *Vanguard Products Corp. v. Parker Hannifin Corp.*, 234 F.3d 1370, 1372 (Fed. Cir. 2000), the defendant argued that during the prosecution of the patent, the inventors viewed a certain process as “fundamental,” and the defendant argued those circumstances imposed the process on the product claims. This Court rejected that argument as well, noting that although the inventors “extolled the economy of manufacture and superior product” made by the process in question, the inventors did not “disclaim[] claim scope beyond products made by [the process].” *Id.* “The method of manufacture, even when cited as advantageous, does not of itself convert product claims into claims limited to a particular process.” *Id.*

Here, based on all the above authority, the district court should have construed the term “dimensionally stable” as a *property* of flexographic plates, not as a *process* by which plates having that property may be made. Instead, as in *AstraZeneca*, the district court drastically limited the scope of the claims of the ’758 patent by reading in certain process limitations because the specification and the prosecution history “emphasized” the importance of annealing. (A091.) But, as discussed in *AstraZeneca* and *Vanguard*, this was clear legal error and warrants

reversal, particularly where there was no express disavowal of claim scope. While the '758 specification and prosecution history certainly discuss the benefits of using certain annealing processes (A068-71), the inventors *never* expressly disclaimed products manufactured by other processes, as would be required by all the authority set forth above to constitute a disavowal of claim scope.

**c. MacDermid Led the District Court Into Error**

At bottom, the district court was led by MacDermid into an erroneous claim construction based on two misperceptions. First, was MacDermid's allegation that the patent allegedly disclosed only one way of making the claimed dimensionally stable plates—the alleged special annealing process—whereby the claims should be so limited. (A065.) This was legal error. As the foregoing authority amply demonstrates, it is well settled that where the patent claim is to a thing, the patent need disclose only one way of making the claimed thing yet still cover the patented thing no matter how made. *See Invitrogen Corp. v. Clontech Labs. Inc.*, 429 F.3d 1052, 1071 (Fed. Cir. 2005).

The second misperception arose from MacDermid's allegation that the claims must be limited to the disclosed manufacturing method because the absence of that method in the prior art was cited by DuPont in responding to PTO allegations that the products described in certain prior art references *inherently met* the stability limitations. (A066; A068-69.) This too was legal error as the

statements in the prosecution history do not rise to the level of a clear and unambiguous disavowal. Instead, the statements were made to show that the prior art plates, which were not annealed—i.e. “absent a critical annealing step”—had not been shown to inherently possess the properties of the flexographic plates claimed by ’758 patent. (See A068; A2303-04.) Such statements were not sufficient to demonstrate that the claims must be read as *requiring* an annealing step. It was the PTO’s burden to establish that a cited reference that does not disclose a claim limitation nonetheless meets it inherently. One way the PTO could have shifted the burden to DuPont on this issue would have been to prove the prior art was made by the same method. *See In re Best*, 562 F.2d 1252, 1255 (C.C.P.A. 1977) (“Where, as here, the claimed and prior art products are identical or substantially identical, or are produced by identical or substantially identical processes, the PTO can require an applicant to prove that the prior art products do not necessarily or inherently possess the characteristics of his claimed product.”). DuPont merely pointed out that the PTO had failed to do that, and that there was no other evidence of inherency. (See A2346-47; A2365-66.)

Further, the district court also pointed to statements made in the applicant’s appeal to the Board of Patent Appeals and the Board’s decision. (A069-71.) But again, such statements were only made to rebut allegations of inherency with respect to the prior art plates. (A2357-66.) And though the Board decision noted

that the prior art plates “have not been subjected to the annealing process disclosed by the appellants,” that fact was only cited in support of the finding that the prior art plates “do not necessarily and inherently possess the appellants’ claimed distortion values.” (A2411.) As such, the statements in the prosecution history do not rise to the level of a clear and unambiguous disavowal of other processes such that the claim should be limited to a particular method of making the claimed flexographic plates.

Accordingly, for all the above reasons, the district court’s construction should be reversed.

**d. The District Court Further Improperly Limited the Annealing Process**

Even if it were proper to import an annealing process limitation into the product claims, the district court’s construction of the claims is not supported by the intrinsic record. In particular, by adopting MacDermid’s claim construction above, the district court further limited the “special annealing” steps such that they *must* be (1) *after* (“subsequent to”) manufacturing of the polymeric film, and (2) *not* part of the process of bonding the photoelastomer layer to the polymeric substrate. (A047; A091.)

Neither of these limitations, however, are supported by the specification or prosecution history. Although the ’758 patent discusses the use of annealing as a process that may achieve the claimed properties, the patent specification and

prosecution history do not limit *when* that process must take place, or require that it be separate from other processes (such as bonding processes). As such, there is no basis to read these additional limitations into the claims even if an “annealing” process limitation is read into the claims. Further, even though prior art processes may not have solved the distortion issue (*see* A047-49), it does not mean that a bonding process conducted using other temperatures and pressures, such as the annealing parameters discussed in the patent, would not resolve the thermal distortion issues noted in the prior art. There is simply no requirement that there be separate bonding and annealing steps.

### **3. The District Court Improperly Resolved Disputed Factual Issues In Evaluating the Accused Products**

Even if this Court were to affirm the district court’s claim construction, it should still vacate the noninfringement holding because genuine issues of material fact remain regarding infringement of the claims by MacDermid’s Digital CST plates.

The district court granted summary judgment of noninfringement solely based on its determination that an adhesive drying step used by MacDermid’s contractor in preparation of its Digital CST plates is not a “special annealing process” as construed by the district court as part of the “dimensional stability” limitation of the claims. (A050-51.) Rather, the district court determined that this adhesive drying step should be considered part of the process of bonding the

photosensitive elastomer to the substrate, a process expressly excluded by the district court's claim construction of the term "dimensionally stable." (*Id.*)

DuPont had, however, provided specific expert evidence demonstrating that the adhesive step was *not* part of the bonding process. (A049; A5663, ¶ 16; *see generally* A5656-708.) DuPont's expert, Dr. James Rice, initially considered the process used by MacDermid to make its digital plates. (A049; A5663-64, ¶¶ 14-16.) MacDermid obtains its substrate material used in its Digital CST plates from a company called Kimoto. (A041; A043; A10837:3-23; A5663-64, ¶ 16.) During the manufacturing process, Kimoto coats the substrate material with a primer and an adhesive, and in between the application of each is a drying step. (A043-44; A5663, ¶ 15; A10837:3-23.) In particular, after applying the adhesive layer, the film goes through a dryer with six different zones with air temperatures ranging from 168-250 °F. (A043; A5664, ¶ 17.) Once dried, the substrate is shipped to MacDermid, and eventually bonded to the photosensitive layer. (A043; A5663-64, ¶ 16.)

Dr. Rice determined via computer modeling analysis of the Kimoto process that the Kimoto process satisfies the "special annealing process" requirements imposed (albeit incorrectly) by the district court's construction. (A5663-74, ¶¶ 16-30.) Dr. Rice determined Kimoto's adhesive drying process is a "special annealing process" because (1) it is in *addition and subsequent* to the heating steps associated

with the manufacture of the substrate; (2) it is *not* the process of bonding; and (3) it satisfies the temperature, tension, and time conditions required by the district court's claim construction. (*Id.*) Specifically, and based on discovery obtained from MacDermid, Dr. Rice explained how the adhesive drying process is *separate* from the bonding process:

After purchasing the primer and adhesive coated film from Kimoto, MacDermid applies a photosensitive elastomer layer to the film. The step of bonding the photosensitive elastomer layer to the film is performed by MacDermid. Thus, the application of a primer and adhesive to the film by Kimoto is not the process of bonding the photosensitive elastomer layer to the polymeric substrate.

(A049; A5633-64, ¶16; A6026-31.) Such evidence, at the minimum, should have created genuine issues of material fact sufficient to avoid summary judgment.

The district court, however, summarily dismissed Dr. Rice's opinions.

(A050.) This it was not entitled to do on summary judgment. *See Frolow*, 710 F.3d at 1310-11 (reversing summary judgment because resolving disagreements in expert testimony is the province of the fact-finder). The issue here is even more compelling than in *Frolow* because MacDermid did *not* offer a competing expert opinion challenging Dr. Rice's evidence that the adhesive drying step is not part of the bonding process. (A041.) It appears that the district court's rejection of Dr. Rice's opinions was based primarily on the court's interpretation of an interrogatory answer relied on by Dr. Rice, and its lay view of the technical features of MacDermid's process. (*See* A050.) This was again improper at the

summary judgment stage when the evidence is required to be viewed in a light most favorable to DuPont and the district court is forbidden from making disputed factual findings. Accordingly, because there are at minimum factual disputes regarding whether the “dimensionally stable” limitation of the ’758 claims (as construed by the district court) are met by Kimoto’s adhesive drying process, the district court’s grant of summary judgment of noninfringement should be reversed for this reason as well.

## **VII. CONCLUSION**

For all of the above reasons, DuPont respectfully submits that this Court should reverse the determinations by the district court on summary judgment that the ’859 patent is invalid for obviousness in view of the prior art and that the ’758 patent is not infringed by MacDermid and remand the case for trial so that the numerous factual disputes can be resolved by the trier of fact in the proper legal context.

Dated: September 18, 2015

Respectfully submitted,

/s/ Charles E. Lipsey

Charles E. Lipsey  
FINNEGAN, HENDERSON, FARABOW,  
GARRETT & DUNNER, LLP  
Two Freedom Square  
11955 Freedom Drive  
Reston, VA 20190-5675  
(571) 203-2700

Howard W. Levine  
Aaron Gleaton Clay  
Finnegan, Henderson, Farabow,  
Garrett & Dunner, LLP  
901 New York Avenue, NW  
Washington, DC 20001-4413  
(202) 408-4000

Jennifer S. Swan  
Jeffrey D. Smyth  
FINNEGAN, HENDERSON, FARABOW,  
GARRETT & DUNNER, LLP  
Stanford Research Park  
3300 Hillview Avenue  
Palo Alto, CA 94304-1203  
(650) 849-6600

Mary K. Ferguson  
FINNEGAN, HENDERSON, FARABOW,  
GARRETT & DUNNER, LLP  
Two Seaport Lane  
Boston, MA 02210-2001  
(617) 646-1600

Charles D. Ossola  
Matthew J. Ricciardi  
VINSON & ELKINS LLP  
2200 Pennsylvania Avenue NW  
Suite 500 West  
Washington, DC 20037-1701  
(202) 639-6500

*Attorneys for Plaintiff-Appellant*

# ADDENDUM

Case 3:06-cv-03383-MLC-TJB Document 651 Filed 06/09/15 Page 1 of 2 PageID: 25998

UNITED STATES DISTRICT COURT  
DISTRICT OF NEW JERSEY

E. I. DU PONT DE NEMOURS AND  
COMPANY,

Plaintiff,

v.

MACDERMID PRINTING SOLUTIONS,  
L.L.C.,

Defendant.

CIVIL ACTION NO. 06-3383 (MLC)

O R D E R

RECEIVED

JUN - 9 2015

AT 8:30 \_\_\_\_\_ M  
WILLIAM T. WALSH  
CLERK

**THE PLAINTIFF**, E. I. du Pont de Nemours and Company

("Plaintiff"), having moved for entry of final judgment pursuant to Fed. R. Civ. P. 54(b) that asserted claims 1, 6, 22, 30, 33, 36, 39, 40, 41, and 48 of the U.S. Patent No. 6,773,859 B2 are invalid as obvious and that asserted claims 1, 3, 4, 7 and 8 of the U.S. Patent No. 6,171,758 B1 are not infringed based upon this Court's Memorandum Opinion and Order dated September 17, 2014, and to stay all remaining claims pending appeal (see dkt. entry. no. 613); and defendant, MacDermid Printing Solutions, L.L.C. ("MacDermid"), opposing the Motion (see dkt. entry no. 614); and

**THE COURT** having reviewed all of the papers submitted upon the Motion; and the Court having held oral argument upon the Motion on May 27, 2015; and, for the reasons stated in the

Case 3:06-cv-03383-MLC-TJB Document 651 Filed 06/09/15 Page 2 of 2 PageID: 25999

opinion on the record on that date, having found that there is no just reason for delay; and for good cause appearing:

**IT IS THEREFORE** on this 9<sup>th</sup> day of June, 2015,

**ORDERED** that Plaintiff's Motion for Entry of Final Judgment pursuant to Fed. R. Civ. P. 54(b) and for a Stay of All Remaining Claims Pending Appeal (see dkt. entry no. 613) is **GRANTED**; and

**IT IS FURTHER ORDERED** that final judgment is hereby entered pursuant to Fed. R. Civ. P. 54(b) that claims 1, 6, 22, 30, 33, 36, 39, 40, 41, and 48 of the U.S. Patent No. 6,773,859 B2 are invalid as obvious and that claims 1, 3, 4, 7 and 8 of the U.S. Patent No. 6,171,758 B1 are not infringed based upon this Court's Memorandum Opinion and Order dated September 17, 2014; and

**IT IS FURTHER ORDERED** that all remaining claims, including MacDermid's claim for attorneys' fees under 35 U.S.C. § 285, are hereby stayed pending appellate review by the United States Court of Appeals for the Federal Circuit.

*Mary L. Cooper*  
MARY L. COOPER  
United States District Judge

UNITED STATES DISTRICT COURT  
DISTRICT OF NEW JERSEY

E.I. DU PONT DE NEMOURS &  
COMPANY,

Plaintiff,

v.

MACDERMID PRINTING  
SOLUTIONS, L.L.C.,

Defendant.

CIVIL ACTION NO. 06-3383 (MLC)

**ORDER & JUDGMENT**

For the reasons stated in the Court's Memorandum Opinion, dated September 17, 2014, **IT IS**, on this 17th day of September, 2014, **ORDERED** that the defendant, MacDermid Printing Solutions, L.L.C.'s ("MacDermid") motion for summary judgment of noninfringement and invalidity of United States Patent No. 6,773,859 B2 (the "'859 Patent") (dkt. entry no. 455) is **GRANTED IN PART AND DENIED IN PART** as follows:

**GRANTED** to the extent MacDermid asserts it is entitled to summary judgment because each of the asserted claims of the '859 Patent (claims 1, 6, 22, 30, 33, 36, 39, 40, 41, and 48) are invalid as obvious; and

**DENIED AS MOOT** to the extent MacDermid claims it is entitled to summary judgment for any other reason; and it is further

**ORDERED** that the plaintiff, E.I. DuPont de Nemours & Company's ("DuPont") motion for summary judgment of infringement of the '859 Patent (dkt. entry no. 464) is **DENIED AS MOOT**; and it is further

**ORDERED** that MacDermid's motion for summary judgment of noninfringement of United States Patent No. 6,171,758 B1 (the "758 Patent") (dkt. entry no. 459) is **GRANTED**; and it is further

**ADJUDGED** that judgment is entered in favor of MacDermid as to DuPont's claims that MacDermid infringes claims 1, 6, 22, 30, 33, 36, 39, 40, 41, and 48 of the '859 Patent; and it is further

**ADJUDGED** that DuPont does not have standing to enforce claims 1, 6, 22, 30, 33, 36, 39, 40, 41, and 48 of the '859 Patent; and it is further

**ADJUDGED** that judgment is entered in favor of MacDermid as to DuPont's assertions that MacDermid infringes claims 1, 3, 4, 7, and 8 of the '758 Patent.

s/ Mary L. Cooper  
**MARY L. COOPER**  
United States District Judge

**NOT FOR PUBLICATION**

UNITED STATES DISTRICT COURT  
DISTRICT OF NEW JERSEY

E.I. DU PONT DE NEMOURS &  
COMPANY,

Plaintiff,

v.

MACDERMID PRINTING  
SOLUTIONS, L.L.C.,

Defendant.

CIVIL ACTION NO. 06-3383 (MLC)

**MEMORANDUM OPINION**

**COOPER, District Judge**

Plaintiff, E.I. DuPont de Nemours & Company (“DuPont”), commenced this action against the defendants, MacDermid, Inc. and MacDermid Printing Solutions, L.L.C. (“MacDermid”), alleging, inter alia, that MacDermid (1) manufactured and sold flexographic printing elements that directly infringe one or more claims of DuPont’s United States Patent No. 6,171,758 B1 (the “‘758 Patent”), (2) encouraged others to directly infringe one or more claims of DuPont’s ‘758 Patent, (3) manufactured and sold flexographic printing elements to be used, treated, processed, or developed in a manner that directly infringes one or more claims of DuPont’s United States Patent No. 6,773,859 B2 (the “‘859 Patent”), and (4) encouraged others to directly infringe one or more claims of DuPont’s ‘859 Patent. See D. Colo. Civ. Action No. 06-816, dkt. entry no. 1, Compl. at ¶¶ 6-9, 14-17.<sup>1</sup>

---

<sup>1</sup> DuPont commenced this action on April 28, 2006 in the United States District Court for the District of Colorado. On July 17, 2006, the United States District Court for the District of Colorado granted the parties’ joint motion to transfer the action to this Court. See id., dkt. entry no. 30, 7-17-06 Order.

The parties present three motions for summary judgment: (1) MacDermid's motion for summary judgment of noninfringement and invalidity of the '859 Patent (the "455 Motion") (see dkt. entry no. 455, Notice of 455 Mot.); (2) DuPont's motion for summary judgment of infringement of the '859 Patent (the "464 Motion") (see dkt. entry no. 464, Notice of 464 Mot.); and (3) MacDermid's motion for summary judgment of noninfringement of the '759 Patent (the "459 Motion") (see dkt. entry no. 459, Notice of 459 Mot.). The Court held oral argument on the motions on November 22, 2013, December 10, 2013, December 16, 2013, and January 27, 2014. For the reasons stated herein, the Court will: (1) grant the 455 Motion in part and deny in part as moot; (2) deny the 464 Motion as moot; and (3) grant the 459 Motion.

## **BACKGROUND**

### **I. Overview of Flexographic Printing Plates**

Flexographic printing plates are used to print images on packaging materials such as flexible films, paper, labels, and cups, as well as newspapers and magazines. (Dkt. entry no. 31, DuPont Appl. for Prelim. Inj. ("DuPont 31 Br.") at 4.) A flexographic printing plate consists of a transparent base layer, a photopolymerizable layer, and a cover sheet. (Id. at 5.) The base layer provides support for the other layers. (Id.) The photopolymerizable layer contains elastomeric binders, monomers, photoinitiators and other additives, and thus, once it is developed, it has a raised surface that depicts the image to be printed. (Id.) A digital flexographic printing plate has an additional infrared ablation layer, which is laminated directly onto the surface of the photopolymerizable layer. (Id.; see dkt. entry no. 44, MacDermid Br. in Opp'n to DuPont Appl. for Prelim. Inj. ("MacDermid 31 Opp'n") at 3 (noting that the

“modern” method of developing a printing plate involves adding a UV absorbing layer directly to the photopolymerizable layer rather than having to place a phototool on top of it.).

To develop an image on a digital flexographic printing plate, the printer must first peel off the cover sheet. (DuPont 31 Br. at 5.) Next, a computer generated infrared laser is moved across the surface of the infrared ablation layer to remove portions of this layer depending upon the digitized image. (Id. at 5-6; MacDermid 31 Opp’n at 3.) As a result, the desired image is transferred onto the infrared ablation layer and a photonegative or “in-situ mask” of the image to be printed is created. (DuPont 31 Br. at 6; MacDermid 31 Opp’n at 3.) The photopolymerizable layer is then exposed to UV light through the in-situ mask. (DuPont 31 Br. at 7; MacDermid 31 Opp’n at 3.) The portions of the infrared ablation layer that were not removed by the infrared laser block parts of the photopolymerizable layer from the UV light. (DuPont 31 Br. at 7; MacDermid 31 Opp’n at 3-4.) The parts of the photopolymerizable layer that are exposed to the UV light polymerize and become insoluble to certain chemical solvents. (DuPont 31 Br. at 7; MacDermid 31 Opp’n at 4 (“Where the UV absorbing layer was removed by the laser, the UV light will cure and harden the photopolymerizable layer.”).) Finally, the printing plate can be washed with chemical solvents and scrubbed with mechanical brushes so that the remaining portions of the infrared ablation layer and the unpolymerized parts of the photopolymerizable layer are removed. (DuPont 31 Br. at 7.) This leaves a raised surface or “printing relief” that can be used to print the desired image. (Id.) Because the flexographic printing plates absorb the chemical solvents, they must undergo a rigorous, lengthy, and costly drying process. (Id. at 9.) This drying step is labor intensive and requires large and expensive drying and emissions control equipment. (Id.)

MacDermid contends that there are a number of alternative methods for removing the remaining portions of the infrared ablation layer and the uncured parts of the photopolymerizable layer, including (1) using water and brushes, (2) using an “air knife” or forced air, and (3) heating the plate to soften the uncured parts and then removing the softened uncured parts with an absorbent material or blotter (*i.e.*, thermal development). (MacDermid 31 Opp’n at 4.) DuPont asserts that its scientists and engineers invented the thermal development process, whereas MacDermid asserts that “DuPont invented nothing.” (See DuPont 31 Br. at 7; MacDermid 31 Opp’n at 4.)

## II. The ‘859 Patent

The ‘859 Patent discloses “a process for preparing a flexographic printing plate from a photosensitive element having a photopolymerizable layer and a thermally removable layer on the photopolymerizable layer.” (Dkt. entry no. 192, 11-19-08 Mem. Op. at 7.) It is comprised of 54 claims, but only claims 1 and 51 are independent. Claim 1 states:

1. A process for making a flexographic printing plate comprising:
  - 1) providing a photosensitive element comprising: at least one photopolymerizable layer on a support comprising an elastomeric binder, at least one monomer, and a photoinitiator, and at least one thermally removable layer disposed above the photopolymerizable layer, the thermally removable layer selected from the group consisting of
    - (a) an actinic radiation opaque layer comprising (i) at least one infrared absorbing material, (ii) a radiation opaque material, wherein (i) and (ii) can be the same or different, and at least one binder having a softening or melting temperature less than 190°C.;
    - (b) a layer of a composition comprising at least one binder and filler, wherein the binder is less than 49% by weight based on the total weight of the binder and filler, and
    - (c) a layer of particulate material having particle size of less than 23 micrometers;

- 2) imagewise exposing the photopolymerizable layer to actinic radiation forming polymerized portions and unpolymerized portions; and
- 3) thermally treating the element of step 2) by heating to a temperature sufficient to remove the thermally removable layer and to remove the unpolymerized portions of the photopolymerizable layer and form a relief.

(Id. at 7-8.)

DuPont introduced its commercial embodiment of claim 1, Digital Cyrel® FAST (“Cyrel”), in 2001. DuPont asserts that Cyrel pioneered and first commercialized the “growing and commercially successful market for the thermal development of digital flexographic printing plates.” In fact, DuPont states that it sold more than \$90 million worth of digital flexographic printing plates that can be thermally developed between 2001 and August of 2006. DuPont also notes that in 2003, Cyrel received the Flexographic Technical Association’s (the “FTA”) “Technical Innovation Award.” (Id. at 8.) MacDermid launched its LAVA products in April 2004. It installed a thermal processing system and began selling its LAVA flexographic printing plates in November 2004. MacDermid has invested over \$4 million in the research and development of its thermal development technology, and has spent over \$797,000 marketing its LAVA products. (Id. at 8-9.) DuPont tested and analyzed MacDermid’s MLT and Magma printing plates in late 2005. DuPont contends that

MacDermid markets its LAVA thermal processing system and equipment and MLT and Magma flexographic printing plates as providing the same benefits and having the same features as DuPont’s Cyrel® FAST thermal technology, describes its infringing technology with a numbering system designed to draw a close parallel in the minds of customers with DuPont’s FAST thermal process equipment, and has even sought a license from DuPont to use the patented technology it is now offering to customers.

(Id. at 9.) DuPont further contends that in addition to copying DuPont’s patented thermal technology, MacDermid has also adopted the same naming conventions for its equipment –

DuPont calls its thermal processing equipment “Cyrel® FAST TD 4260” and MacDermid calls its thermal processing equipment “LAVA 4260.” (Id.)

### **III. The Prosecution History of the ‘859 Patent**

The original application for the ‘859 Patent was filed with the United States Patent and Trademark Office (“PTO”) on February 27, 2002. (Id.) The patent application listed “Roxy Ni Fan, et al.” as the inventors and “a process for making a flexographic printing plate and a photosensitive element for use in the process” as the patent’s title. (Id.) The applicants filed an Information Disclosure Statement with the application, which informed the PTO about the existence of (1) United States Patent Nos. 3,060,024, 3,060,025, 3,264,103, 4,429,027, 5,175,072 (“Martens ‘072 Patent”), 5,262,275 (“Fan ‘275 Patent”),<sup>2</sup> 5,607,814, 5,719,009, 5,840,463, and 5,888,697, and (2) European Patent Nos. 0665469, 0665471, and 0741330 (the “Fan ‘330 Publication”). (Id. at 9-10) Also, the applicants filed a Supplemental Information Disclosure Statement on February 24, 2003 disclosing the existence of United States Patent Application No. 2002/0009672 (“Daems ‘672 Patent Application”). (Id. at 10.)<sup>3</sup>

The PTO issued an Office Action in which the patent examiner (1) allowed claims 51-54, (2) rejected claims 1-7, 9-10, 14-16, 18, 28-30, 33-42, and 45-50, and (3) objected to claims 8, 11-13, 17, 19, 31-32, and 43-44. (Id.) The patent examiner stated that he was rejecting claims 1-7, 9-10, 14-16, 18, 28-30, 33-42, and 45-50 because they were either

---

<sup>2</sup> We refer to these patents using the name of the first patentee or applicant listed on the Information Disclosure Statement in conjunction with the patent’s last three numbers.

<sup>3</sup> The Daems ‘672 Patent Application is “[n]on-provisional of provisional application No. 60/214,016, filed on Jun. 26, 2000.” (Id.) The Daems ‘672 Patent Application was filed on January 24, 2002, approximately one month before the ‘859 Patent application was filed. (Id.)

anticipated under 35 U.S.C. § (“Section”) 102(a) and (e), or obvious under Section 103(a) in light of the Daems ‘672 Patent Application. (Id.) The patent examiner explained that the Daems ‘672 Patent Application:

discloses processes using elements comprising photopolymerizable layers containing elastomeric binders overcoated with thermally removable layers comprising binders, infrared absorbing materials and opaque materials within the scope of the thermally removable layers of paragraph “a” of the instant claims. The thermally removable layer is thermally imaged to form a mask and then the element is photopolymerized and thermally treated to remove unpolymerized areas and the thermally removable opaque layers. If [the Daems ‘672 Patent Application] do[es] not anticipate the instant claims, then it would at least be obvious to one skilled in the art to select thermally removable layers, photopolymerizable layers, thicknesses and processing temperatures from the generic disclosure in [the Daems ‘672 Patent Application] in order to carry out the processes of [the Daems ‘672 Patent Application].

(Id.) The patent examiner also explained that claims 8, 11-13, 17, 19, 31-32, and 43-44 were only objectionable because they depended on rejected claims, and thus, they would be allowed if written in independent form. (Id. at 10-11.)

The applicants responded to the Office Action on March 29, 2004. In addition to the response, the applicants submitted a declaration by co-inventor Adrian Lungu, which showed that the claimed invention had been completed in the United States on or before June 9, 1999. (Id. at 11.) The applicants thus asserted that the Daems ‘672 Patent Application was “no longer available for use as a reference in rejecting the present claims” because the claimed invention predated the filing of the Daems ‘672 Patent Application. (Id.) Accordingly, the applicants (1) alleged that the claimed invention was not anticipated or obvious to one skilled in the art, and (2) requested that the patent examiner reconsider the rejection of certain claims.

(Id.)

The PTO then issued a Notice of Allowability, which allowed claims 1 through 51.

The form used to transmit the issue fee and publication fee, which was received by the PTO on April 22, 2004, lists DuPont as the assignee of the ‘859 Patent. The PTO issued the ‘859 Patent on August 10, 2004. (Id.)

#### **IV. The ‘758 Patent**

The PTO issued the ‘758 Patent, entitled “Dimensionally Stable Flexographic Printing Plates,” on January 9, 2001. (See dkt. entry no. 459-3, Ex. DD, ‘758 Patent.) The abstract states:

The present invention is a flexographic printing plate having a very low degree of thermal distortion during development. This flexographic printing plate comprises a dimensionally stable substrate and an image bearing relief layer, wherein the thermal distortion of the flexographic printing plate in both the machine and the transverse directions is less than 0.02% when the plate is developed at temperatures in the range from about 100° C. to about 180° C.

(Id.)

The ‘758 Patent is comprised of 21 claims, but only claims 1 and 19 are independent. (See id. at cols. 8-10.) Claim 1 states:

**1. A photosensitive plate suitable for use as a flexographic printing plate comprising a dimensionally stable, flexible, polymeric substrate and a photosensitive elastomer layer, wherein the plate has a thermal distortion in both the machine and the transverse directions which is less than 0.03% when the plate is exposed to actinic radiation and, after exposure, is developed at temperatures between 100 and 180° C.**

(Id. at col. 8, lines 18-25.)

#### **V. The Prosecution History of the ‘758 Patent**

The application leading to the ‘758 Patent was filed in November 1994. (Id.) In an Office Action mailed in March 1995, the PTO examiner found the claims subject to a

restriction or election requirement. (Dkt. entry no. 310, 3-15-10 Mem. Op. & Order at 4.)

After the applicants filed a response in April 1995, the examiner rejected the claims in an Office Action mailed in June 1995. The applicants traversed the rejections in a response filed in August 1995. The examiner finally rejected the claims in a November 1995 Office Action. The applicants submitted an amendment and response in January 1996. (Id.) They then appealed to the Board of Patent Appeals and Interferences (“Appeals Board”). (Id. at 4-5.)

The applicants submitted a brief defending the patent claims, which was received in April 1996. The examiner also submitted an answer defending the rejections. In a decision mailed on June 29, 2000, the Appeals Board disagreed with the examiner and allowed the patent to be issued. (Id. at 5.) The ‘758 Patent was issued on January 9, 2001.

## **DISCUSSION**

### **I. Applicable Legal Standards**

#### **A. Summary Judgment Standard**

Motions for summary judgment are governed by Rule 56, which provides that the Court “shall grant summary judgment if the movant shows that there is no genuine dispute as to any material fact and the movant is entitled to judgment as a matter of law.” Fed.R.Civ.P. 56(a). The movant has the initial burden of proving the absence of a genuinely disputed material fact relative to the claims in question. Celotex Corp. v. Catrett, 477 U.S. 317, 330 (1986). Material facts are those “that could affect the outcome” of the proceeding, and “a dispute about a material fact is ‘genuine’ if the evidence is sufficient to permit a reasonable jury to return a verdict for the non-moving party.” Lamont v. New Jersey, 637 F.3d 177, 181 (3d Cir. 2011) (quoting Anderson v. Liberty Lobby, Inc., 477 U.S. 242, 248 (1986)). The

burden on the movant may be discharged by pointing out to the district court that there is an absence of evidence supporting the nonmovant's case. See Celotex, 477 U.S. at 323.

If the movant demonstrates an absence of genuinely disputed material facts, then the burden shifts to the nonmovant to demonstrate the existence of at least one genuine issue for trial. See Matsushita Elec. Indus. Co., Ltd. v. Zenith Radio Corp., 475 U.S. 574, 586–87 (1986); Williams v. Borough of W. Chester, Pa., 891 F.2d 458, 460–61 (3d Cir. 1989). “Where the record taken as a whole could not lead a rational trier of fact to find for the non-moving party, there is no genuine issue for trial.” Matsushita Elec. Indus. Co., 475 U.S. at 587 (internal quotation marks omitted). The nonmovant cannot, when demonstrating the existence of issues for trial, rest upon argument; the nonmovant must show that such issues exist by referring to the record. See Fed.R.Civ.P. 56(c)(1).

When determining whether a genuine dispute of material fact exists, the Court must view the evidence in the light most favorable to the nonmovant and draw all reasonable inferences in that party's favor. Scott v. Harris, 550 U.S. 372, 380 (2007); Wishkin v. Potter, 476 F.3d 180, 184 (3d Cir. 2007). If the nonmovant fails to demonstrate that at least one genuine dispute exists for trial, then the Court must determine whether the movant is entitled to judgment as a matter of law. See McCann v. Unum Provident, 921 F.Supp.2d 353, 357 (D.N.J. 2013). “A movant is entitled to judgment as a matter of law if, at trial, no reasonable jury could find for the non-moving party.” Id.

## **B. Infringement Standard**

Determination of a claim of infringement involves a two-step inquiry. First, the patent claim is construed, a question of law in which the scope of the asserted claim is defined.

Markman v. Westview Instruments, Inc., 52 F.3d 967, 979 (Fed.Cir. 1995). Second, the claim, as construed, is compared to the allegedly infringing product to determine whether the product contains every limitation contained in the claim or the substantial equivalent of any limitation not literally present. Laitram Corp. v. Rexnord, Inc., 939 F.2d 1533, 1535 (Fed.Cir. 1991) (noting that “the failure to meet a single limitation is sufficient to negate infringement of the claim”).

There is a ““heavy presumption’ that a claim term carries its ordinary and customary meaning.” CCS Fitness Inc. v. Brunswick Corp., 288 F.3d 1359, 1366 (Fed.Cir. 2002). The ordinary and customary meaning of a claim term is the meaning a “person of ordinary skill in the art in question” would give to such term on the effective filing date of the patent application. Phillips v. AWH Corp., 415 F.3d 1303, 1313 (Fed.Cir. 2005). Such a person is deemed to interpret the claim term in the context of the entire patent, including the specification. Id. A claim term should generally be given its ordinary meaning unless the patentees “clearly set forth a definition of the disputed claim term in either the specification or prosecution history.” CCS Fitness Inc., 288 F.3d at 1366. Thus, words in a claim are generally given their ordinary and customary meanings in the absence of a contrary indication in the patent specification or file history. Wolverine Worldwide, Inc. v. Nike, Inc., 38 F.3d 1192, 1196 (Fed.Cir. 1994).

When interpreting an asserted patent claim, the Court should look first to the intrinsic evidence of record, which includes the patent’s claims, specification, and complete prosecution history. Markman, 52 F.3d at 979. Such intrinsic evidence is the most significant source of the legally operative meaning of disputed claim language. Vitronic Corp. v.

Conceptronic, Inc., 90 F.3d 1576, 1583 (Fed.Cir. 1996). In reviewing this intrinsic evidence, the Court considers the context in which a term is used both within the claim at issue and within the claims that are not at issue. Phillips, 415 F.3d at 1314. Further, the Court must interpret claim terms in light of the specification. Id. at 1315 (noting that the specification is “highly relevant” to claim construction and usually dispositive).

The Court, in addition to reviewing the specification, should also consider the patent’s prosecution history. Id. at 1317; Graham v. John Deere Co., 383 U.S. 1, 33 (1966) (“It is, of course, well settled that an invention is construed not only in the light of the claims, but also with reference to the file wrapper or prosecution history in the Patent Office.”). The doctrine of “prosecution history estoppel” requires that a patent’s claims be interpreted in light of all PTO proceedings that occurred during the patent application process. Festo Corp. v. Shoketsu Kinzoku Co., Ltd., 535 U.S. 722, 733 (2002) (noting that “prosecution history estoppel” ensures that claims are interpreted in light of those claims that were cancelled or rejected). Accordingly, the prosecution history is useful in claim construction because it demonstrates how the inventor limited the invention during the course of the patent prosecution, and thus, narrowed the scope of the ultimately patented product. Phillips, 415 F.3d at 1317. Nevertheless, because the prosecution history reflects the ongoing negotiations between the inventor and the PTO, it is often less clear and less useful than the specification. Id.

The ordinary meaning of claim language as understood by a person of skill in the art will be readily apparent to a lay judge in some instances, after reviewing the intrinsic evidence, and claim construction will involve simply applying the widely accepted meanings of commonly understood words. Id. at 1314. In such circumstances, general purpose dictionaries

may be helpful. Id. However, “heavy reliance on the dictionary divorced from the intrinsic evidence risks transforming the meaning of the claim term to the artisan into the meaning of the term in the abstract, out of its particular context, which is the specification.” Id. at 1321.

### **C. Standards Governing Patent Validity**

A patent is presumed to be valid, and each of its claims are presumed valid independent of the validity of other claims. 35 U.S.C. § 282(a). A party asserting the invalidity of a patent or one or more of its claims must establish such invalidity by clear and convincing evidence. Bausch & Lomb, Inc. v. BarnesHind/Hydrocurve, Inc., 796 F.2d 443, 446 (Fed.Cir. 1986).

#### **1. Anticipation**

35 U.S.C. § 102 states that a claimed invention is invalid for anticipation where, inter alia,

- (a) the claimed invention was patented, described in a printed publication, or in public use, on sale, or otherwise available to the public before the effective filing date of the claimed invention; or
- (b) the claimed invention was described in a patent . . . , or in an application for patent published or deemed published . . . , in which the patent or application, as the case may be, names another inventor and was effectively filed before the effective filing date of the claimed invention.

35 U.S.C. § 102(a)-(b).

“Although anticipation under 35 U.S.C. § 102 is a question of fact, it may be decided on summary judgment if the record reveals no genuine dispute of material fact.” Golden Bridge Tech., Inc. v. Nokia, Inc., 527 F.3d 1318, 1321 (Fed.Cir. 2008). The test for anticipation is the same two-step process used in determining infringement: a court must, first,

construct the claims, and second, compare the patented invention to the prior art. See Int'l Seaway Trading Corp. v. Walgreens Corp., 589 F.3d 1233, 1239 (Fed.Cir. 2009); Bristol-Myers Squibb Co. v. Ben Venue Labs., Inc., 246 F.3d 1368, 1378 (Fed.Cir. 2001) (“[T]hat which would literally infringe if later anticipates if earlier.”).

## 2. Obviousness

A patent is invalid for obviousness “if the differences between the claimed invention and the prior art are such that the claimed invention as a whole would have been obvious before the effective filing date of the claimed invention to a person having ordinary skill in the art to which the claimed invention pertains.” 35 U.S.C. § 103.

The Court must employ an expansive and flexible approach to the question of obviousness. KSR Int'l Co. v. Teleflex Inc., 550 U.S. 398, 401 (2007). In determining whether a claimed invention was obvious, the Court must objectively consider (1) the scope and content of the prior art, (2) the differences, if any, between the prior art and the claims at issue, and (3) the level of ordinary skill in the pertinent art. Graham v. John Deere Co. of Kansas City, 383 U.S. 1, 17 (1966). The Court should also analyze secondary considerations of nonobviousness such as the patented invention’s commercial success, whether the patent satisfied a long-felt but unmet need, and whether the invention received industry praise. See id. at 17-18. “It is black letter law that the ultimate question of obviousness is a question of law.” Richardson-Vicks Inc. v. Upjohn Co., 122 F.3d 1476, 1479 (Fed.Cir. 1997). The issue turns on whether the claimed subject matter, as a whole, would have been obvious to a person of ordinary skill at the time the invention was made. See KSR Int'l Co., 550 U.S. at 420. “Where . . . the content of the prior art, the scope of the patent claim, and the level of ordinary

skill in the art are not in material dispute, and the obviousness of the claim is apparent in light of these factors, summary judgment is appropriate.” Id. at 427.

When a patent combines elements known in the prior art “with each performing the same function it had been known to perform and yields no more than one would expect from such an arrangement, the combination is obvious.” Id. at 417 (quotation and citation omitted); see id. at 416 (“[W]hen a patent claims a structure already known in the prior art that is altered by the mere substitution of one element for another known in the field, the combination must do more than yield a predictable result.”). When the prior art teaches away from a particular combination of known elements, however, the successful combination of those elements is less likely to be obvious. Id. That a patent combines elements known in the prior art in accord with their established functions does not, alone, make the patent obvious. Id. at 418. Rather, the Court should also “identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the elements in the way the claimed new invention does.” Id.

A patent may be proved obvious by showing that the combination of known elements was obvious to try. Id. at 421. “When there is a design need or market pressure to solve a problem and there are a finite number of identified, predictable solutions, a person of ordinary skill has good reason to pursue the known options within his or her technical grasp.” Id. Thus, a predictable success from one of these options likely results from ordinary skill and common sense, rather than innovation. Id. In such a situation, that the combination of known elements was obvious to try may sufficiently show that the combination was obvious under Section 103. Id.

### 3. Best Mode

A patent specification “shall set forth the best mode contemplated by the inventor or joint inventor of carrying out the invention.” 35 U.S.C. § 112(a). Compliance with the best mode requirement is a question of fact. Green Edge Enters., LLC v. Rubber Mulch Etc., LLC, 620 F.3d 1287, 1296 (Fed.Cir. 2010). The sufficiency of the disclosure of the best mode is determined as of the filing date. Id. A patent is invalid if its inventor fails to comply with the best mode requirement.

Determining compliance with the best mode requirement is a two-pronged inquiry. “First, the court must determine whether, at the time the patent application was filed, the inventor possessed a best mode of practicing the claimed invention.” Id. “This inquiry is wholly subjective and addresses whether the inventor must disclose any facts in addition to those sufficient for enablement.” U.S. Gypsum Co. v. Nat'l Gypsum Co., 74 F.3d 1209, 1212 (Fed.Cir. 1996); see also Green Edge Enters., 620 F.3d at 1296 (stating that first prong is subjective and “focuses on the inventor’s personal preferences as of the application’s filing date”). “Second, if the inventor has a subjective preference for one mode over all others, the court must then determine whether the inventor ‘concealed’ the preferred mode from the public.” Green Edge Enters., 620 F.3d at 1296. The second prong examines – in the event the inventor had a best mode of practicing the claimed invention – “whether the specification adequately disclosed what the inventor contemplated as the best mode so that those having ordinary skill in the art could practice it.” See U.S. Gypsum Co., 74 F.3d at 1212. This inquiry is objective and “depends upon the scope of the claimed invention and the level of skill in the relevant art.” See Green Edge Enters., 620 F.3d at 1296.

## II. The '455 Motion

MacDermid argues that it is entitled to summary judgment because: (1) each of claims 1, 6, 22, 30, 33, 36, 39, 40, 41, and 48 (the “asserted claims of the ‘859 Patent”) are invalid as obvious; (2) United States Patent Nos. 5,925,500 (the “‘500 Patent”) and 5,322,761 (the “‘761 Patent”) anticipated various asserted claims of the ‘859 Patent; (3) each asserted claim of the ‘859 Patent is invalid for a failure to disclose the best mode; (4) no reasonable juror could find MacDermid directly or indirectly infringes the asserted claims of the ‘859 Patent; and (5) DuPont cannot meet its burden of proof on damages. (See generally dkt. entry no. 457, MacDermid 455 Br.)

### A. Obviousness Analysis

MacDermid contends that the asserted claims are invalid as obvious, as “[e]ach asserted claim is an obvious combination of known elements performing their respective function.” (Id. at 20.) That is, “the asserted claims include a method for creating a flexographic printing plate that combined two known technologies – digital imaging and thermal development.” (Id. at 20-21.) MacDermid further argues:

Digital imaging had been known and described in the patent literature since at least 1993 and had been commercially available in this country since 1997. Thermal development was first described in the patent literature in 1966 and had been commercialized one month before the time of invention. The combination simply selected the best techniques amongst very limited options to be used in one sequential process. No change or alteration needed to be made to the digital plates or the thermal process to thermally develop digital plates. Additionally, the prior art described heat and wash development as alternative and interchangeable development methods. Further, it was known that non-meltable particles were thermally removable because the particles get “carried along” with “wicked” polymer. Moreover, the prior art contained disclosures explicitly suggesting the combination.

(Id. at 21.)

## 1. The Scope and Content of the Prior Art

The Court considers the scope and content of the prior art as it existed on June 9, 1999.

(See 11-19-08 Mem. Op. at 11 (finding that claimed invention had been completed in the United States on or before June 9, 1999).) Prior art is limited to analogous references “from the same field of endeavor” as the claimed invention; if not within the same field of endeavor, a reference may be prior art if it is reasonably pertinent to the particular problem the inventor of the claimed invention was addressing. See In re Bigio, 381 F.3d 1320, 1325 (Fed.Cir. 2004).

### a. The Martens '072 Patent

The PTO issued the Martens '072 Patent, entitled “Flexographic Printing Plate Process,” on December 29, 1992. (See dkt. entry no. 455-2, Robinson Decl., Ex. 11, Martens '072 Patent (listing the filing date as July 26, 1990).) The “Description of the Invention” section of the Martens '072 Patent states that the

process of the present invention for producing a flexographic printing plate comprises providing a relief imageable element comprising a flexible substrate which can transmit ionizing radiation, said substrate having on one surface thereof a radiation hardenable composition in a thickness of at least 0.3 mm, imagewise irradiating said composition to harden the composition in irradiated areas, contacting said imagewise irradiated layer with an absorbent layer which can absorb unirradiated composition when it has been heated between 40°C. and 200°C., heating said composition layer to a temperature between 40°C. and 200°C. while it is in contact with said absorbent layer, said temperature being sufficiently high so as to enable said composition in unirradiated areas to be absorbed by said absorbent layer (usually by flowing into said absorbent layer), allowing at least 75% by weight of said composition (which is unirradiated) in unirradiated areas to be absorbed by said absorbent layer, and removing said absorbent layer and said at least 75% by weight of composition from said flexible substrate, the process further comprising the step of irradiating said composition layer through the substrate with ionizing radiation to harden some but less than all of said composition layer and thereby form a hardened zone

between said flexible substrate and unhardened composition before said at least 5% of said composition is allowed to be absorbed by said absorbent layer.

(Id. at col. 5, lines 7-34.) The Martens '072 Patent thus describes a process for developing flexographic printing plates using heat, rather than solvents. (See id. col. 10, lines 29-38; col. 13, lines 62-67 (stating that the invention describes a process through which flexographic printing plates are developed without use of solvents).) This was an analog (not digital) thermal plate that had a release layer. (See dkt. entry no. 602, 12-16-13 Hr'g Tr. at 7:12-15.)

The specification of the Martens '072 Patent explains that after imagewise exposure to actinic radiation, the uncured portions of the elastomer layer must be removed. (Id. at col. 12, lines 42-45.) The specification instructs that the uncured portions of the elastomer be removed by heating the uncured elastomer to a temperature sufficient to cause melting and pressing an absorbent sheet material against the uncured elastomer. (Id. at col. 12, lines 45-58.) The contact between the molten uncured elastomer and the absorbent sheet material results in “a transfer of the uncured elastomer from the planar contiguous layer to the absorbant [sic] sheet material.” (Id. at col. 12, lines 56-64.) The absorbent sheet material is then removed, leaving the relief structure. (Id. at col. 12, lines 61-64.)

#### **b. The Fan '275 Patent**

The PTO issued the Fan '275 Patent, entitled “Flexographic Printing Element Having an IR Ablatable Layer and Process for Making a Flexographic Printing Plate,” on November 16, 1993. (See dkt. entry no. 455-4, Robinson Decl., Ex. 14, Fan '275 Patent (listing the filing date as August 7, 1992).) The “Summary of the Invention” section of the Fan '275 Patent states that:

The present invention relates to a photosensitive printing element used for preparing flexographic printing plates comprising

- (a) a support,
- (b) a photopolymerizable layer comprising an elastomeric binder, at least one monomer and an initiator having sensitivity to non-infrared actinic radiation, said layer being soluble, swellable or dispersible in a developer solution prior to exposure to actinic radiation,
- (c) at least one barrier layer which is soluble, swellable, dispersible or liftable in the developer solution for the photopolymerizable layer prior to exposure to actinic radiation, and
- (d) at least one layer of infrared radiation sensitive material which is substantially opaque to actinic radiation wherein the infrared-sensitive material is ablative from the surface of the barrier layer upon exposure to infrared laser radiation.

The invention further relates to a process for making a flexographic printing plate, which comprises:

- (1) imagewise ablating layer (d) of the element described above with infrared laser radiation to form a mask;
- (2) overall exposing the photosensitive element to actinic radiation through the mask; and
- (3) treating the product of step (2) with at least one developer solution to remove (i) the infrared-sensitive material which was not removed during step (1), (ii) the areas of the barrier layer which were not exposed to actinic radiation, and (iii) the areas of the photopolymerizable layer (b) which were not exposed to actinic radiation.

(Id. at col. 2, lines 13-44.) The Fan '275 Patent thus relates to flexographic printing plates comprised of a support, a photopolymerizable layer, and an ablation layer, as well as the process for making such plates. (See id.; see also id. at col. 2, lines 49-54 (explaining that invention combines "the convenience and sensitivity of infrared laser imaging with conventional photopolymerizable compositions to produce flexographic printing plates with known good printing quality quickly, economically, and by digital imaging means").)

According to DuPont, the Fan '275 Patent was the first digital imaging patent. (See 12-16-13 Hr'g Tr. at 8:10-23.)

The specification of the Fan '275 Patent generally describes the process of the invention as involving: (1) the formation of a mask by imagewise ablating the infrared radiation sensitive material comprising layer (d); (2) "overall exposing the photosensitive element to actinic radiation through the mask"; and (3) developing the product of step (2) using a developer solution. (Id. at col. 8, lines 60-68; see also id. at col. 9, line 4 to col. 10, line 58.) The specification instructs that the infrared sensitive layer, layer (d), "should be capable of absorbing infrared radiation and should be opaque to actinic radiation." (Id. at col. 5, lines 56-58.) Layer (d) also may include a binder, if desired. (Id. at col. 5, lines 59-60.) The specification further explains that during the imagewise ablating step, "material in the infrared-sensitive layer is removed, i.e., ablated, in the areas exposed to the infrared laser radiation." (Id. at col. 9, lines 19-21.) The photosensitive element is then overall exposed to actinic radiation through the mask, resulting in both polymerized and unpolymerized portions. (Id. at col. 9, lines 32-43.)

### **c. The '761 Patent**

The PTO issued the '761 Patent, entitled "Flexographic Printing Plate Having a Vanadium Oxide Antistatic Coating Layer," on June 21, 1994. (See Robinson Decl., Ex. 12, '761 Patent (listing the filing date as June 4, 1992).) The "Abstract" section of the '761 Patent states: "A flexographic printing plate comprising in the following order: a flexible substrate, a photohardenable composition, and a colloidal vanadium oxide antistatic layer. The antistatic layer provides protection from static induced defects until and after the flexographic plate is processed." (Id.) The "Detailed Description" section of the '761 Patent states, in pertinent part:

The present invention relates to a flexographic printing plate comprising a, radiation hardenable composition (radiation polymerizable, radiation curable, or radiation cross-linkable) as a layer on a flexible substrate, the substrate also containing an antistatic layer of vanadium oxide above the radiation curable layer. Other antistatic layers may be used in combination with the vanadium oxide antistatic layer. The plate is imagewise irradiated to harden the radiation curable (hardenable) composition in irradiated areas. Said imagewise irradiated layer may then be wash developed or preferably contacted with an absorbent layer which can absorb (or wick) unirradiated composition when the composition has been heated between 40° and 200° C. The composition layer is heated so that it is at a temperature between 40° and 200° C. while in contact with said absorbent layer, the temperature being sufficiently high to enable said composition in unirradiated areas to flow into said absorbent layer. At least 75% of said composition in unirradiated areas in contact with said absorbent layer is absorbed by said absorbent layer, and by removing said absorbent layer, said at least 75% of composition from unirradiated areas is removed from said flexible substrate. The at least 75% removal is accomplished in at least one and up to ten steps of contact and heating with an absorbent material. . . . The actual temperatures will vary with the specific substrate and composition used. Preferably at least 80% of the unirradiated composition is removed from the areas heated in contact with the absorbent layer. More preferably at least 90 or at least 95% is removed. The hardening or curing step of the process (by irradiation) can also act to increase the adhesion of the composition to the substrate.

(Id. at col. 7, line 65 to col. 8, line 23; col. 8, lines 42-49.)

The '761 Patent thus describes a process where (1) a flexographic printing plate is imagewise exposed, and (2) the imagewise irradiated layer is then developed with either solvents or heat. (See id.)

#### **d. The Fan '330 Publication**

The European Patent Office published the Fan '300 Publication, entitled "Flexographic element having an infrared ablative layer and process for making a flexographic printing plate," on November 24, 1999. (See dkt. entry no. 455-5, Robinson Decl., Ex. 15, Fan '300 Publ'n at 1 (listing filing date as February 23, 1996).) The "Field of

the Invention" section of the Fan '300 Publication states: "This invention relates to a process for making a flexographic printing plate from a photosensitive printing element, particularly a flexographic element having an infrared radiation ablative layer capable of being selectively removed by a laser beam." (Id. at 2, lines 5-9.)

The "Summary of the Invention" section of the Fan '300 Publication states:

In accordance with this invention there is provided

(1) a photosensitive element for use as a photopolymer printing plate, comprising:

(a) a support;

(b) at least one layer of a photopolymerizable material on the support, the photopolymerizable material comprising at least one elastomeric binder, at least one monomer, at least one initiator having sensitivity to non-infrared actinic radiation, and optionally at least one plasticizer, wherein at least one of the monomer and the optional plasticizer is a low molecular weight material; and

(c) at least one infrared ablation layer which is ablative by infrared radiation and substantially opaque to non-infrared actinic radiation, said infrared ablation layer being in direct contact with the at least one layer of photopolymerizable material (b) and having a surface opposite the photopolymerizable layer (b) capable of being exposed to laser ablation, the infrared layer comprising:

(i) at least one infrared absorbing material;

(ii) a radiation opaque material, wherein (i) and (ii) can be the same or different; and

(iii) at least one binder which is substantially incompatible with at least one of the low molecular weight materials of layer (b) and which is selected from polyamides, copolymers of ethylene and vinyl acetate, hydroxyalkyl cellulose, cellulose acetate butyrate, polybutyral, cyclic rubbers, nitroglycerine, polyacetals, polyimides, polycarbonates, polyesters, polyalkylenes, polyphenylene ethers, polyethylene oxides, polylactones, and combinations thereof; and optionally,

(d) a coversheet;

wherein the infrared ablation layer is tack-free or substantially tack-free on the photopolymerizable layer and is ablative from the surface of the photopolymerizable layer upon exposure to infrared laser radiation after removal of the coversheet, if present, and

(2) a process for making a flexographic photopolymer printing plate from the photosensitive element described in (1) above.

(Id. at 4, lines 16-46.) Thus, the Fan '300 Publication relates to flexographic photopolymer printing plates comprised of a support, a coversheet, a photopolymerizable layer, and an ablation layer, as well as the process for making such plates. (See id.)

## **2. The Differences Between the Prior Art and the Claims at Issue**

The Fan '275 Patent and the Martens '072 Patent were known to persons skilled in the art in 1999, the year in which the claimed invention was made. (See dkt. entry no. 46-6, Mahanna Decl., Ex. 2, part 5, at G-1 to G-5, 3-29-04 Resp. & Lungu Decl. (stating that the claimed invention was conceived and reduced to practice in 1999).) See KSR Int'l Co., 550 U.S. at 424 (noting that the District Court was correct to perform the obviousness analysis as of the time the patentee designed the subject matter in the claim). The '859 Patent describes the same technology and processes pertaining to digital imaging of flexographic printing plates as disclosed in the Fan '275 Patent, including (1) a photosensitive element comprising a support, a photopolymerizable layer, and a third layer consisting of an infrared absorbing material, a radiation opaque material, and a binder, (2) ablation of an imagewise ablative layer using infrared laser radiation to form a mask, (3) overall exposure of the photopolymerizable layer to actinic radiation through the mask, resulting in polymerized and unpolymerized portions of the photopolymerizable layer, and (4) development by removing

the unpolymerized portions of the photopolymerizable layer. (Compare Robinson Decl., Ex. 13, '859 Patent at col. 5, lines 57-61, col. 11, lines 13-41, col. 17, lines 21-60, col. 20, lines 22-47, and col. 43, lines 14-36, with Robinson Decl., Ex. 14, Fan '275 Patent at col. 2, lines 13-44, 55-58, col. 5, lines 56-62, col. 9, lines 4-53, and col. 10, lines 21-24.) The '859 Patent furthermore discloses the same process of thermal development of flexographic printing plates as was disclosed in the Martens '072 Patent. Specifically, both patents disclose the use of heat to form the relief by removing the unpolymerized portions of the photopolymerizable layer after imagewise exposure to actinic radiation. (Compare Robinson Decl., Ex. 13, '859 Patent at col. 20 lines 22-67, col. 21, lines 1-55, and col. 43, lines 37-40, with Robinson Decl., Ex. 11, Martens '072 Patent at col. 5, lines 7-34, and col. 12, lines 42-67.)

The parties dispute whether it would have been obvious to one skilled in the art to essentially “unite old elements” by combining the digital imaging technology disclosed in the Fan '275 Patent with the thermal development technology described in the Martens '072 Patent. See KSR Int'l Co., 550 U.S. 415-16 (“[A] patent for a combination which only unites old elements with no change in their respective functions . . . obviously withdraws what is already known into the field of its monopoly and diminishes the resources available to skillful men.” (internal quotation marks omitted)). The digital imaging technology and the thermal development technology described in the '859 Patent perform the same functions they had been known to perform and yield a predictable result. See id. at 417 (emphasizing that a combination of known elements “with each performing the same function it had been known to perform and yield[ing] no more than one would expect from such an arrangement” is obvious (quotation and citation omitted)). The flexographic printing plate is digitally imaged

using laser radiation on an imagewise ablative layer, exposed to actinic radiation through the mask, and then developed using known thermal development processes. (See Robinson Decl., Ex. 13, '859 Patent at col. 17, line 21 to col. 18, line 2; col. 18, line 50-55; col. 20, line 29 to col. 21, line 48.)

That said, DuPont argues that

[n]either DuPont nor its expert, Dr. Cakmak, disputes that the prior art contained various “digital solvent” references (e.g., the [Fan] ‘275 Patent, the [Fan] ‘330 Publication, DuPont’s DPU plate, and MacDermid’s CBU plates) that disclosed steps 1(a) and 2 of claim 1 of the ‘859 Patent. None, however, disclosed or suggested the “thermal developing” step; rather, the prior art taught forming a relief only by washout with solvents or aqueous solutions. Similarly, neither DuPont nor Dr. Cakmak dispute that the prior art contained various “analog thermal” references (e.g., the [Martens] ‘072 Patent, the ‘761 Patent, and the ‘471 Patent) that disclosed one or more layers above a photopolymerizable layer. However, the prior art did not teach or suggest the compositions recited in parts 1(a)-(c) of claim 1 of the ‘859 Patent, nor did the prior art teach or suggest that the layers above the photopolymerizable layer were thermally removable. Indeed, at the time the invention was made, the only “analog thermal” development process still required a solvent wash to clean up the floor and remove fine particles.

(See dkt. entry no. 504, DuPont 455 Opp’n Br. at 19 (footnotes omitted).)

DuPont further argues that “[a] person of ordinary skill in the art would have had no reason to believe thermal development of a digital plate would yield a useful result.” (Id. at 20.) DuPont states that in May through July of 1999, “there were only two commercially available ways to develop flexographic printing plates – washing with solvent solutions and washing with aqueous (i.e., water-based) solutions.” DuPont thus argues that, because DuPont did not commercialize its analog thermal development process until the following

year, “‘thermal’ was not a ‘known option’ for commercial development of even analog plates at the time of the invention.” (See id.)<sup>4</sup>

DuPont also argues that MacDermid’s assertion – that “the claimed invention not only represents a simple substitution but it constitutes a combination of the best options available at the time” – is incorrect, as “one of ordinary skill would not have known that industry demand for digital imaging could best be met by thermal development.” (Id. at 21.) DuPont insists this is the case because “there still existed questions about whether thermal development could provide all of the stated environmental and time savings benefits.” (Id. at 21-22.) DuPont moreover insists that “the solvent-based market was still growing at an accelerated rate [in 1999] and there were no existing thermal customers so one of ordinary skill would have been unmotivated to introduce a technology to its digital customers that provided few tangible benefits over the solvent processing workflow that these customers were already using.” (Id. at 22 (internal quotation marks omitted).)

DuPont further argues that its expert, Dr. Mukerrem Cakmak, concluded that “one of ordinary skill would not have expected that the combination of digital solvent references, and their laser ablation layers, would be thermally removable” and that “the references relied upon by MacDermid’s experts provide no support for their conclusion that there existed a high degree of predictable success that this combination would work.” (Id.)

---

<sup>4</sup> DuPont notes that “thermal development techniques known at the time still required a final solvent wash to ‘clean up’ the plate, further reducing the motivation to ‘try’ thermal development because one of ordinary skill would not have expected it to solve the environmental and production time problems associated with solvent-based processes.” (Id. at 21.)

DuPont finally argues that “the prior art did not contain any teachings of alternative development methods for an analog plate that would have suggested to one of ordinary skill in the art that existing digital solvent plates could be alternatively thermally developed.” (*Id.* at 22-23.)

The KSR Court has instructed that

a patent composed of several elements is not proved obvious merely by demonstrating that each of its elements was, independently, known in the prior art. Although common sense directs one to look with care at a patent application that claims as innovation the combination of two known devices according to their established functions, it can be important to identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the elements in the way the claimed new invention does. This is so because inventions in most, if not all, instances rely upon building blocks long since uncovered, and claimed discoveries almost of necessity will be combinations of what, in some sense, is already known.

KSR Int'l Co., 550 U.S. at 418 (emphasis added). The KSR Court additionally noted that a patent claim can be proven obvious merely by showing that the combination of elements was “obvious to try.” See id. at 421. The KSR Court stated:

When there is a design need or market pressure to solve a problem and there are a finite number of identified, predictable solutions, a person of ordinary skill has good reason to pursue the known options within his or her technical grasp. If this leads to the anticipated success, it is likely the product not of innovation but of ordinary skill and common sense. In that instance the fact that a combination was obvious to try might show that it was obvious under [35 U.S.C.] § 103.

(*Id.*)

The Court finds that there are several reasons that would have prompted a person of ordinary skill to combine digital imaging technology and thermal development technology in the same way as the ‘859 Patent. In May 1999, there existed only two imaging techniques

(analog and digital) and four development techniques (solvent, water, air knife, and heat plus a blotter). (See MacDermid 455 Br. at 31.)<sup>5</sup> As this Court previously found, digital imaging has several benefits over analog imaging, including that phototools are expensive and time-consuming to make. (See 11-19-08 Mem. Op. at 68-69.) At the time of the invention, digital plates were only commercially developed by solvents. (See MacDermid 455 Br. at 31.) Thermal development conversely has multiple advantages over solvent development, including that it is faster, less expensive, and does not create environmental issues regarding the use and disposal of solvents. (See 11-19-08 Mem. Op. at 69; see also MacDermid 455 Br. at 31.) A person of ordinary skill in the field therefore would be motivated to combine digital imaging and thermal development in one sequential process to gain the benefits of both technologies. (See 11-19-08 Mem. Op. at 69.) See generally KSR Int'l Co., 550 U.S. at 418 (emphasizing importance of identifying “a reason that would have prompted a person of ordinary skill in the relevant field to combine the elements in the way the claimed new invention does”).

As was the case in KSR, here there was a “finite number of identified, predictable solutions,” thus, “a person of ordinary skill ha[d] good reason to pursue the known options within his or her technical grasp.” See KSR Int'l Co., 550 U.S. at 421; see also Ortho-McNeil Pharm., Inc. v. Mylan Labs., Inc., 520 F.3d 1358, 1364 (Fed.Cir. 2008) (stating that “KSR posits a situation with a finite, and in the context of the art, small or easily traversed,

---

<sup>5</sup> DuPont argues that thermal was not a “known option” for commercial development at the time of the invention. (See DuPont 455 Opp'n Br. at 20.) The Court, however, notes that one of ordinary skill in the art is presumed to be aware of prior art beyond that of which is commercialized. See McNeil-PPC, Inc. v. L. Perrigo Co., 337 F.3d 1362, 1369-70 (Fed.Cir. 2003).

number of options that would convince an ordinarily skilled artisan of obviousness").<sup>6</sup>

MacDermid moreover describes in detail why digital imaging and thermal development were not only known options, but the best options available at the time:

As of May 1999, digital imaging was well known, commercially successful, and growing. In a July 1997 article, two named inventors (Fan/Taylor) emphasized “digital plates print finer highlights, while retaining deep shadows, and with lower dot gain than conventional printing throughout the tonal range. Color reproduction on press is brighter, more dynamic, and can achieve a larger process color gamut.” ([Dkt. entry no. 457-10, Robinson Decl., Ex. 23, Fan/Taylor Article]; [dkt. entry no. 457-2, Robinson Decl., Ex. 2, Rule 30(b)(6) Dep. of DuPont] at 113:4-9). Digital plates are a “truly superior product” gaining “worldwide acceptance” and “[o]rders for digital plate materials and digital plate exposure devices are steadily increasing.” Id. Therefore here, as in KSR, there existed a marketplace at the time of invention that created a “strong incentive” for the ordinarily skilled artisan to expand the use, availability and marketability of digital plates. KSR, 550 U.S. at 424 (“Technological developments made it clear that engines using computer-controlled throttles would become standard.”); Muniauction, Inc. v. Thomson Corp., 532 F.3d 1318, 1326-27 (Fed. Cir. 2008) (public speech touted desirability of World Wide Web and motivated combination).

At the same time, May 1999, thermal development had been known since the 1960’s, 3M patents detailed its utility and benefits in the 1990’s, and DuPont commercialized an analog-thermal system at a U.S. tradeshow in April 1999, one month earlier. DuPont detailed the benefits of thermal over solvent at this tradeshow, and characterized thermal as revolutionary” and “breakthrough technology.” ([Dkt. entry no. 457-13, Robinson Decl., Ex. 35, CMM 99 Press Briefing]; [dkt. entry no. 455-12, Robinson Decl., Ex. 37, Cyrel Article]; [Rule 30(b)(6) Dep. of DuPont] at 174:8-176:18).

As a result, there existed at the time of invention a marketplace with known design incentives that created a “strong incentive” to expand the use and

---

<sup>6</sup> DuPont argues that the commercial failure of analog thermal plates taught away from combining digital and thermal technologies. (See 12-16-13 Hr’g Tr. at 50:22 – 51:2; 67:24 – 68:3.) The Court, however, agrees with MacDermid that the Martens ‘072 Patent contains an example that describes an “excellent rendition” of an image using an analog thermal plate. (See Martens ‘072 Patent at col. 21, line 19 to col. 22, line 2.)

availability of the “revolutionary” thermal process, by combining it with the “truly superior” digital plates. One only needed to place a “truly superior” digital plate (after imagewise exposure) into a “revolutionary” thermal process. Alternatively, one needed to only upgrade an analog-thermal plate in a known manner to become a digital-thermal plate. Given the design incentives and market demands at the time of invention, one of ordinary skill would have had not just “a reason” – but good and compelling reasons – to combine digital imaging with thermal development. Ecolab, Inc. v. FMC Corp., 569 F.3d 1335, 1349-50 (Fed. Cir. 2009) (using known technique to improve known process was obvious); Leapfrog Enterprises, Inc. v. Fisher-Price, Inc., 485 F.3d 1157, 1161-62 (Fed. Cir. 2007) (upgrading device to employ modern electronics was obvious).

(MacDermid 455 Br. at 33-34.) The Court adopts the analysis set forth by MacDermid regarding the market forces. Because of these market forces, the finite number of options, and the benefits of both digital imaging and thermal development, the Court finds that the combination of the two technologies would be obvious to one of ordinary skill in the art.

### **3. The Level of Ordinary Skill in the Pertinent Art**

The obviousness analysis is conducted from the perspective of a person of ordinary skill in the prior art. See 35 U.S.C. § 103. The hypothetical person of ordinary skill “is an objective legal construct who is presumed to be aware of all the relevant prior art.” Janssen Pharmaceutica N.V. v. Mylan Pharm., Inc., 456 F.Supp.2d 644, 653 (D.N.J. 2006), aff’d, 233 Fed.Appx. 999 (Fed.Cir. 2007). The person of ordinary skill “is also a person of ordinary creativity, not an automaton.” KSR Int’l Co., 550 U.S. at 421. MacDermid defers to DuPont’s conclusion that one of ordinary skill in the prior art “possesses a B.S. degree in chemistry or chemical engineering and 3-5 years experience with photopolymer printing plate formulations and applications, or an individual having an advanced technical degree in another discipline and 3-5 years experience with photopolymer printing plate formulations

and applications.” (See dkt. entry no. 455-2, Robinson Decl., Ex. 8, Cakmak ‘859 Patent Expert Report at ¶22; MacDermid 455 Br. at 26.)

#### **4. Secondary Considerations of Non-obviousness**

Secondary considerations of objective evidence of non-obviousness include evidence of long-felt but unmet need, failures of others, commercial success, copying, unexpected results, and industry acclaim. As MacDermid has succeeded in establishing a *prima facie* case of obviousness, the Court will consider these indicia of non-obviousness. DuPont relies on three secondary considerations of objective evidence of non-obviousness: (1) commercial success; (2) long-felt but unmet need; and (3) industry praise. (See DuPont 455 Opp’n Br. at 23-27.)<sup>7</sup>

##### **a. Commercial Success**

DuPont argues that its Cyrel – the commercial embodiment of the invention claimed in the ‘859 Patent – “was an immediate commercial success, generating more than \$90 million in sales from its introduction in 2001 through 2006.” (See *id.* at 24.) DuPont further argues that [s]ales in 2002 grew by an astonishing 988% percent and continued to grow thereafter, by 242% in 2003, by 350% in 2004, by 148% in 2005, and by 31% through August 2006. Sales of DuPont’s thermally developable digital printing plates (i.e., those described and claimed in the ‘859 Patent) grew at a much faster rate than sales of traditional solvent-developed plates, evidencing that the increased sales were driven by the novel thermal development capability and not overall grown [sic] in the flexography market.

(*Id.*)

---

<sup>7</sup> DuPont only mentions these three secondary considerations in its brief. The Court notes that DuPont discussed other secondary considerations at oral argument. While the Court considered all of the secondary considerations proffered by DuPont both in its brief and at oral argument, the Court finds it necessary to remark only on those discussed *infra*.

MacDermid conversely argues that commercial success is probative only if there is a nexus between the claimed invention and the commercial success. (MacDermid 455 Br. at 39-40.) MacDermid states that DuPont cannot establish a nexus because, inter alia, DuPont is unable to show that Cyrel's success is not the result of features of the claimed invention already in the prior art. (See id. at 40-41.)

The Court first notes that DuPont's argument sensationalizes Cyrel's commercial success. DuPont offers the declaration of the Director of Sales and Marketing for DuPont's Color Proofing Business in North America, Robert M. Zoelle. (See DuPont 455 Opp'n Br. at 24 (citing dkt. entry no. 32, Zoelle Decl. at ¶¶ 11-25).) DuPont insists that Cyrel "was an immediate commercial success," yet Zoelle himself conceded in his declaration that "marketplace acceptance [of Cyrel] was not immediate." (See Zoelle Decl. at ¶ 18.) In fact, it was only through "work[ing] with initial customers to install [Cyrel] equipment . . . and provid[ing] them with [Cyrel] material for evaluation," that DuPont was able to "develop a market for thermally developed plates" "over time." (See id.)

DuPont also provides many growth figures, but fails to put those figures into context. DuPont claims that Cyrel has generated "more than \$90 million in sales," but DuPont does not document more revealing statistics, such as its profit. (See DuPont 455 Opp'n Br. at 24.) DuPont further illustrates Cyrel's growth figures, but fails to mention that all thermally developed plates – including others besides Cyrel – "account for only about 13% of the overall market in the United States for flexographic printing plates." (See Zoelle Decl. at ¶ 19.)<sup>8</sup>

---

<sup>8</sup> The Court notes that Zoelle's declaration was filed in 2006, so thermally developed plates may have gained additional market share by the date of this memorandum opinion.

The Court finds that the evidence proffered by DuPont regarding Cyrel's commercial success is insufficient to overcome MacDermid's strong showing of obviousness. DuPont provides only simple sales figures, which do little to assist the Court in gauging Cyrel's commercial success. The Court also notes that DuPont's market share in the flexographic printing plate market reduces the impact that any probative evidence could have on establishing commercial success. See Geo. M. Martin Co. v. Alliance Mach. Sys. Int'l LLC, 618 F.3d 1294, 1305 (Fed.Cir. 2010). DuPont does not adequately establish a nexus between the claimed invention and its purported commercial success, other than utilizing attorney argument to briefly explain that the benefits customers may realize through their adoption of Cyrel. (See DuPont 455 Opp'n Br. at 25.)

**b. Long-Felt but Unmet Need**

DuPont argues that because digital imaging of flexographic printing plates was first patented in 1992, there was a seven year period where digital plates were not being thermally developed. DuPont argues that the '859 Patent solved this problem and brought the benefits of thermal processing to digital plates. (See DuPont 455 Opp'n Br. at 25.) DuPont concludes that after the commercial success of Cyrel, MacDermid acknowledged that "the market has spoken and the need is clear." (See 12-16-13 Hr'g Tr. at 15-20.) Nothing about DuPont's argument, however, demonstrates that there was a palpable need for digital thermal plates and that such a need existed for a long time. The Court therefore finds that DuPont fails to establish a long-felt but unmet need.

### c. Industry Praise

DuPont argues that it received industry awards and praise from the FTA, as it was the 2003 recipient of the FTA's "Technical Innovation Award." (See DuPont 455 Opp'n Br. at 25.) DuPont states that it received the award "for the environmental improvements, speed, and superior quality of its new [Cyrel] system." (*Id.*) MacDermid argues that the FTA's "Technical Innovation Award" is awarded on the basis of innovation and not invention. (See MacDermid 455 Br. at 51-52.)

While the Court finds that the FTA award may be at least some evidence of industry praise, it is vastly insufficient to overcome MacDermid's strong showing of obviousness. As stressed by MacDermid, the FTA's "Technical Innovation Award" awards innovative technology in the flexographic industry. (See *id.* at 52.) According to the award's entry guidelines and application, "[t]he definition of innovation is 'the act of introducing something new.' It should not be confused with invention, which is the act of producing or contriving something previously unknown. So the application, marketing and development of new or existing technology would be considered innovative technology." (Dkt. entry no. 455-16, Robinson Decl., Ex. 62, Flexographic Technical Innovation Award Brochure). As such, this example of industry praise is limited to praising Cyrel as an innovation, not an invention. The Court also notes that – as with the commercial success factor – DuPont's market share in the overall flexographic printing product industry somewhat reduces the impact that this evidence could have on establishing industry praise. See Geo. M. Martin Co., 618 F.3d at 1305.

**B. Conclusion on Obviousness**

The Court finds that MacDermid has carried its burden of proving by clear and convincing evidence that the asserted claims of the '859 Patent are invalid as obvious over the prior art references. The Court will therefore grant MacDermid's motion for summary judgment of invalidity of those claims of the '859 Patent. The Court will issue an appropriate order and judgment.

**III. The 464 Motion**

Because the Court finds that the '859 Patent is invalid on the grounds of obviousness under 35 U.S.C. § 103, the Court need not consider DuPont's motion for summary judgment of infringement of the '859 Patent. The Court will therefore deny the 464 Motion as moot. The Court will issue an appropriate order and judgment.

**IV. The 459 Motion**

MacDermid moves for summary judgment of noninfringement of claims 1, 3, 4, 7, and 8 (the "asserted claims of the '758 Patent") of the '758 Patent. (See Notice of 459 Mot; dkt. entry no. 460, MacDermid 459 Br.) DuPont asserts that MacDermid's Digital CST plate literally infringes each of the asserted claims of the '758 Patent. (See dkt. entry no. 503, DuPont 459 Opp'n Br. at 1.)

MacDermid states that "the Court is presented with the narrow question of whether a genuine issue of material fact exists with respect to literal infringement of the asserted claims by Digital CST," and that "[n]o such issue even remotely exists with respect to this contrived

claim.” (MacDermid 459 Br. at 2.)<sup>9</sup> MacDermid notes that DuPont has no evidence Digital CST meets two requirements of the asserted claims. (Id.) That is, MacDermid argues that (1) Digital CST does not include “a dimensionally stable, flexible, polymeric substrate,” as construed by the court, and (2) the undisputed evidence shows Digital CST distorts more than 0.03% in at least one direction when developed at temperatures between 100° and 180° Celsius. (See id. at 2-3.)

In regard to the first argument, MacDermid contends that the adhesive drying process used by its contractor, Kimoto, does not meet the Court’s construction because it is not a “special annealing process” that “controls” the “dimensional stability” of the substrate.<sup>10</sup> Instead, MacDermid argues that Kimoto’s adhesive drying process is an essential aspect of the process of bonding the photosensitive elastomer layer to the substrate, explicitly excluded by the Court’s construction of the ‘758 Patent. MacDermid argues that Dr. James Rice’s opinion does not create a genuine issue of material fact as to whether the Kimoto adhesive drying process is a “special annealing process” under the Court’s claim construction. (See generally id.)

---

<sup>9</sup> MacDermid states that while DuPont initially claimed all products capable of thermal development infringed the asserted claims, DuPont now alleges that only Digital CST infringes claims 1, 3, 4, 7, and 8 of the ‘758 Patent. (See MacDermid 459 Br. at 1.) MacDermid states that DuPont is no longer asserting that MacDermid’s Digital MAX, Digital MVP, Digital MLT, and Digital Magma flexographic printing plates infringe the claims of the ‘758 Patent. (See id.) MacDermid further contends that when the case was filed in April 2006, it only sold Digital MLT and Digital Magma. (See id.) Digital CST, MacDermid states, was not sold until 2007 and did not exist when the Complaint was filed. (See id.)

<sup>10</sup> Kimoto’s adhesive drying process is explained infra.

DuPont asserts, in response, that: (1) the Court's claim construction does not preclude a finding that Kimoto's adhesive drying process is a "special annealing process"; (2) MacDermid's attempt to read claim 1 of the '758 Patent to require less than 0.03% distortion at every point in the claimed range of 100° to 180° Celsius goes far beyond the Court's claim construction and is a misreading of the claim; (3) MacDermid's attempt to conflate adhesive drying of the Digital CST plates by Kimoto into MacDermid's manufacturing process of bonding the photopolymer to the substrate finds no support in the Court's construction; and (4) MacDermid wrongly presumes that the "special annealing process" required by the Court's construction must "control" thermal distortion. (See DuPont Opp'n Br. at 1-4.)<sup>11</sup>

In its Reply Brief, MacDermid supplements its initial arguments with the following points: (1) adhesive drying is not "special" or "annealing"; (2) adhesive drying is an essential step in the multi-step process of bonding the substrate to the photosensitive layer; (3) a "dimensionally stable" substrate must have its dimensional stability controlled by a special annealing process; and (4) according to DuPont's expert's test results, Digital CST distorts more than 0.03% in at least one direction when developed at 170° Celsius (*i.e.*, between 100-180° Celsius). (See dkt. entry no. 524, MacDermid 459 Reply Br.)

#### **A. Background – MacDermid's Digital CST Plate**

DuPont alleges that MacDermid infringes claims 1, 3, 4, 7, and 8 of the '758 Patent by making, selling, and using its Digital CST plates in the United States. (See DuPont 459

---

<sup>11</sup> DuPont also initially argued that MacDermid's attacks on the admissibility and reliability of Dr. Rice's opinions are unfounded, but this Court already ruled on this issue. (See generally dkt. entry no. 608, 6-30-14 Order.)

Opp'n Br. at 5.) The Court adopts MacDermid's description of the manufacturing process of its Digital CST plate:

Digital CST is manufactured in three gauges, 45, 67 and 107 mils. The manufacturing process for Digital CST begins with the manufacture of the polymeric substrate. Digital CST 45 uses Melinex 943 (7 mil) for its flexible polymeric substrate. Melinex 943 is a polyethylene terephthalate ("PET") film manufactured by DuPont-Teijin. Melinex 943 has been manufactured in this country with the same process since 1982. DuPont-Teijin does not subject Melinex 943 to a special annealing process.

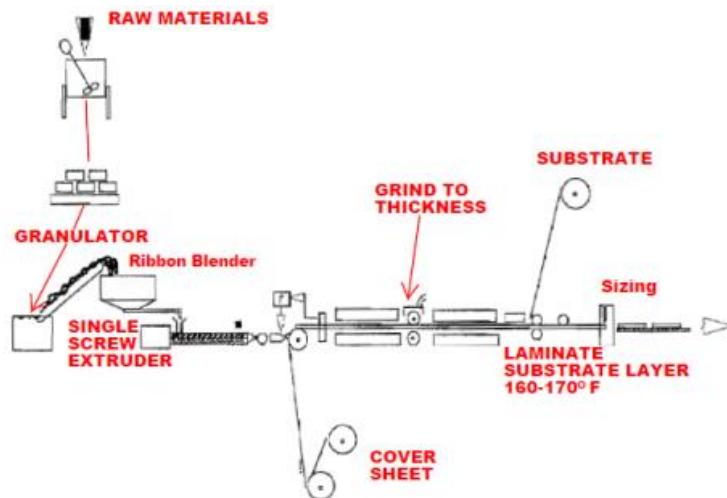
Digital CST 67 and 107 use Hostaphan 4407 (5 mil) for the flexible polymeric substrates. Hostaphan 4407 is a PET film manufactured by Mitsubishi Polyester Film, Inc. Hostaphan 4407 has been manufactured with the same process in this country since 1982. Mitsubishi does not subject Hostaphan 4407 to a special annealing process.

MacDermid manufactures Digital CST on what is referred to as Line A. Line A products require application of a primer layer (PVDC) and an adhesive layer (ADB10R) onto the substrate before the substrate is placed on the manufacturing line. Because MacDermid does not have the capability of applying the primer and adhesive on Line A, it contracts with Kimoto to perform this step in the bonding process. Thus, once the PET films that are used for Digital CST are manufactured by DuPont-Teijin or Mitsubishi, they are shipped to Kimoto to be coated with the primer and adhesive layers.

On Line 2, Kimoto coats a primer (PVDC) onto the substrate at Coating Station No. 1, and then dries the primer in Dryer No. 1. On the same line, immediately thereafter, Kimoto coats an adhesive (ADB10R) onto the dried primer at Coating Station No. 2 and dries the adhesive in Dryer No. 2. Dryer No. 2 has six zones operating with air temperatures ranging from 168 - 250° F (75.5 to 121.1° C). Line 2 was installed in 1992 and has been operational ever since.

After coating and drying the primer and adhesive layers onto the PET film, Kimoto ships the film to MacDermid where MacDermid completes the manufacture of Digital CST on Line A. There, on Line A, MacDermid laminates the photosensitive layer to the adhesive coated surface of the substrates. Specifically, melted photopolymer is first extruded onto the coversheet as it is wound around a casting roll. The photopolymer is cooled

and ground by an abrasive roll to the desired thickness. Next, the PET substrate, which is already coated with PVDC and ADB10R, is laminated to the photopolymer surface by two rollers heated to between 160 and 170° F. A schematic of Line A is below:



(MacDermid 459 Br. at 4-7. (internal citations and footnote omitted).) MacDermid also notes that “DuPont contends the ‘special annealing’ purportedly occurs only in one zone of Kimoto’s Dryer No. 2, specifically Zone 3. The air temperature of Zone 3 is 250° F.” (*Id.* at 6 n.1.)

## B. Infringement Analysis

As the Court discussed supra, the determination of a claim of infringement involves a two-step inquiry. First, the patent claim is construed, a question of law in which the scope of the asserted claim is defined. Markman, 52 F.3d at 979. Second, the claim, as construed, is compared to the allegedly infringing product to determine whether the product contains every limitation contained in the claim or the substantial equivalent of any limitation not literally present. Laitram Corp., 939 F.2d at 1535 (noting that “the failure to meet a single limitation is sufficient to negate infringement of the claim”).

## 1. The Asserted Claims of the '758 Patent and the Court's Construction

Step one in the infringement inquiry involves construing the patent claim. Markman, 52 F.3d at 979. The '758 Patent is composed of 21 claims, but only claims 1 and 19 are independent. (See '758 Patent at cols. 8-10.) Claim 1 states:

**1.** A photosensitive plate suitable for use as a flexographic printing plate comprising a dimensionally stable, flexible, polymeric substrate and a photosensitive elastomer layer, wherein the plate has a thermal distortion in both the machine and the transverse directions which is less than 0.03% when the plate is exposed to actinic radiation and, after exposure, is developed at temperatures between 100 and 180° C.

(Id. at col. 8, lines 18-25.)

Claim 1 requires that the photosensitive plate include “a dimensionally stable, flexible, polymeric substrate.” (See id. at col. 8, lines 19-20.) The Court previously construed “dimensionally stable” to mean:

A flexible polymeric substrate whose dimensional stability has been controlled through a special annealing process, namely an annealing process that: (1) is in addition and subsequent to the heat treating steps associated with manufacturing the polymeric film, (2) is not the process of bonding the photosensitive elastomer layer to the polymeric substrate, and (3) comprises: (i) heating the substrate to a temperature above its glass transition temperature but below its melting temperature and at or greater than the temperature to which the substrate is later subjected during thermal development, (ii) at tensions of less than 200 psi, and (iii) for a time greater than the time required to bring the film to the annealing temperature, such that a specially annealed substrate has less thermally induced distortion than a non-specially annealed substrate.

(3-15-10 Mem. Op. & Order at 11-12, 20, 40.)

## 2. Comparison of Construed Claim to Allegedly Infringing Product

The Court then moves to step two of the infringement inquiry, which involves comparing the claim, as construed, to the allegedly infringing product to determine whether the product contains every limitation contained in the claim or the substantial equivalent of any limitation not literally present. Laitram Corp., 939 F.2d at 1535. The Court finds that MacDermid did not infringe the asserted claims of the '758 Patent because Kimoto's adhesive drying process is not a "special annealing process." See id. (holding that "the failure to meet a single limitation is sufficient to negate infringement of the claim"); see also 3-15-10 Mem. Op. & Order at 11-12, 20, 40 (noting that to be dimensionally stable, substrate must undergo special annealing process).

MacDermid argues that Kimoto's adhesive drying process cannot satisfy the Court's construction because:

(1) drying an adhesive layer onto a substrate is not a "special annealing process," (2) adhesive drying is an essential aspect of what the Court specifically excluded, namely the process of bonding the photosensitive elastomer layer to the substrate, and (3) the undisputed evidence shows Kimoto does not "control" the dimensional stability of the substrates.

(MacDermid 459 Br. at 10.) DuPont responds by arguing that

Kimoto's adhesive drying process is a "special annealing process" because (1) it is in addition and subsequent to the heating steps associated with the manufacture of the substrate (a fact that MacDermid does not dispute); (2) it is not the process of bonding (a fact that MacDermid disputes); and (3) it satisfies the temperature, tension, and time conditions (a fact that MacDermid disputes only on the basis that DuPont's evidence allegedly is inadmissible).

(DuPont 459 Opp'n Br. at 10.)

During claim construction, this Court held that “the process of bonding the photosensitive elastomer layer to the polymeric substrate” is not a “special annealing process.” (See 3-15-10 Mem. Op. & Order at 40.) As such, if Kimoto’s adhesive drying is part of the bonding process, then it cannot be a “special annealing process.”

In construing “dimensionally stable” during claim construction, the Court looked to “clear and unambiguous statements regarding the annealing process made in both the specification and over the course of the prosecution history.” (See 3-15-10 Mem. Op. & Order at 20.) The Court noted that

the patent specification repeatedly highlights the importance of annealing. The specification even states that “[t]he desirability of such semicrystalline polymers arises from the discovery that dimensional stability of these polymer substrates may be controlled through a special annealing process.” (‘758 Patent at col. 2, lines 55-59.) In addition to mentioning different annealing methods, the specification explains this annealing process, focusing on temperature, tension, and time. (Id. at col. 2, lines 59-67, col. 3, lines 1-26.) The specification then provides four examples, in which the crucial distinguishing feature of the testing was whether the tested samples were in fact subjected to annealing. (Id. at col. 5, lines 26-66, col. 6, lines 1-67, col. 7, lines 1-67, col. 8, lines 1-16.)

(Id. at 16.) The ‘758 Patent not only describes controlling the dimensional stability of polymer substrates through a special annealing process, but it also mentions an optional step that may be taken to “surface treat[] [the substrate] for better adhesion.” (See ‘758 Patent at col. 3, line 66 to col. 4, line 5.) The ‘758 Patent states:

The substrate optionally may be surface treated for better adhesion. Examples of surface treatments include coating the surface with MSOL (an amorphous silica with silane coupling agent) as described in U.S. Pat. No. 5,204,219 [the “‘219 Patent”] or corona treating the surface followed by use of a primer such as an aziridene, as described in U.S. Pat. No. 5,187,044 [the “‘044 Patent”].

(Id.) Both of the enumerated patents illustrate using heat to dry an adhesive coating onto a

substrate. (See dkt. entry no. 459-3, Ex. II, '044 Patent at col. 17, line 61 to col. 18, line 9; dkt. entry no. 459-3, Ex. JJ, '219 Patent at col. 7, line 42 to col. 8, line 13.) The '758 Patent therefore differentiates between annealing the substrate and heating it for "better adhesion."

MacDermid also argues that "[t]he ['758 Patent] examples confirm adhesion techniques are not the invention's 'special annealing process.'" (MacDermid 459 Br. at 14.) MacDermid specifically points to example 3 in the '758 Patent, which discusses flexographic printing plates that were produced using various PEN film substrates. (See '758 Patent at col. 6, lines 62-63.) In example 3, three plates were annealed at 170° C. for five minutes, and four plates were not annealed. (See *id.* at 62-67.) All seven plates were coated with a primer as disclosed by the '044 Patent. The results demonstrate that "the plates produced from the annealed PEN films have lower distortion than do plates produced with unannealed substrates." (*Id.* at col. 7, lines 21-24.) The Court considered this during claim construction and found it significant to construing "dimensional stability." (See 3-15-10 Mem. Op. & Order at 16.)

MacDermid also argues that:

The Court's [claim construction] ruling also found the prosecution history showed the applicants (DuPont) had distinguished the claimed invention by emphasizing the "whole notion of annealing." (*Id.*, p. 17[.]) The Court marshaled the prosecution history and found applicants repeatedly rejected the Examiner's position that Martens and Prioleau taught the claimed invention. (*Id.*, p.17-20[.]) Indeed, even though Martens and Prioleau created plates by drying adhesives onto the substrate before lamination, the applicants repeatedly argued the plates of Martens and Prioleau were not subjected to the "critical," "further" and "important" annealing step that "enables one to achieve the very low degrees of distortion."

For example, the Court noted the applicants responded to the examiner's obviousness rejection, by stating:

The concept that all flexographic printing plates, including those disclosed in Martens and Prioleau, will have some “inherent” degree of thermal distortion, does not overcome Martens’ and Prioleau’s lack of teaching or suggestion as to the importance or desirability of dimensional stability. There is no basis for the inference that the inherent degree of distortion in Martens’ and Prioleau’s plates is in the range claimed. In fact, the Examples in the specification show that absent a critical annealing step, many polymeric films, including PEN and PET films, and plates made from such films do not meet the low distortion levels claimed in the present invention.

(MacDermid 459 Br. at 15-16 (citing 3-15-10 Mem. Op. & Order at 17-18).)<sup>12</sup> The Court concurs with MacDermid’s analysis and finds that this weighs against DuPont’s contention that adhesive drying constitutes a “special annealing process.”

In arguing that Kimoto’s adhesive drying process is not part of the bonding process, DuPont proffers the following statement made by Dr. Rice in his expert report:

After purchasing the primer and adhesive coated film from Kimoto, MacDermid applies a photosensitive elastomer layer to the film. The step of bonding the photosensitive elastomer layer to the film is performed by MacDermid. Thus, the application of a primer and adhesive to the film by Kimoto is not the process of bonding the photosensitive elastomer layer to the polymeric substrate.

(Dkt. entry no. 460-9, Robinson Decl., Ex. K, part 1, Expert Report of Dr. James Rice at ¶ 16 (footnotes omitted).) Dr. Rice’s sole foundation for this statement is MacDermid’s answer to DuPont’s Interrogatory No. 17, wherein MacDermid allegedly did not mention the Kimoto adhesive drying process. (See id. (citing to MacDermid’s Supp. Resp. to Third Set of

---

<sup>12</sup> MacDermid provides several additional examples of DuPont emphasizing – in the prosecution history – the importance of the annealing process. (See MacDermid 459 Br. at 16-17.)

Interrogs.).) There is, however, no support for this statement in MacDermid's answer to DuPont's Interrogatory No. 17, as MacDermid explicitly mentions in its answer that the PET substrate is "coated with an adhesive layer." (See dkt. entry no. 503-1, Ossola Decl., Ex. D, MacDermid's Supp. Resp. to Third Set of Interrogs. at 8.) The Court finds that Dr. Rice's opinion does not create a genuine issue of material fact as to whether the Kimoto adhesive drying process is a "special annealing process" under the Court's claim construction.

Although Dr. Rice proffered a conclusory opinion that Kimoto's adhesive drying process is not part of the bonding process, he testified that the primer and the adhesive are placed on the substrate by Kimoto "[f]or later bonding of the photosensitive layer." (See dkt. entry no. 460-11, Robinson Decl., Ex. O, Rice Dep. 256:13-20.) When asked if "there is any other reason for putting the primer and adhesive on the substrates," Dr. Rice answered, "[n]ot that I know of." (Id. at 257:6-9.) Although this is not an admission on behalf of Dr. Rice that Kimoto's adhesive drying process is a distinct part of the bonding process, Dr. Rice nonetheless confesses that the two are at least related.

### **C. Conclusion on Infringement**

The Court holds that MacDermid's Digital CST plates do not infringe the '758 Patent. Digital CST does not contain every limitation contained in claim 1 of the '758 Patent because its dimensional stability is not controlled through a "special annealing process," as is required by the Court's claim construction. (See 3-15-10 Mem. Op. & Order at 40.) See Laitram Corp., 939 F.2d at 1535. Specifically, Kimoto's adhesive drying process is not a "special annealing process" that "controls" the "dimensional stability" of the substrate. Kimoto's adhesive drying, rather, is more properly considered a part of the process of bonding the

photosensitive elastomer layer to the substrate, a process that is explicitly excluded by the Court's construction of the '758 Patent. The Court therefore will grant MacDermid's motion for summary judgment of noninfringement. The Court will issue an appropriate order and judgment.

s/ Mary L. Cooper  
**MARY L. COOPER**  
United States District Judge

Dated: September 17, 2014

**NOT FOR PUBLICATION**UNITED STATES DISTRICT COURT  
DISTRICT OF NEW JERSEY

:

E.I. DU PONT DE NEMOURS & COMPANY, :  
Plaintiff, : CIVIL ACTION NO. 06-3383 (MLC)  
v. :  
MACDERMID, INC., et al. :  
Defendants. :  
:

---

**COOPER, District Judge**

Several terms in two patents concerning flexographic printing plates are at issue here. The plaintiff, E.I. du Pont de Nemours & Company ("DuPont"), alleges that the defendant MacDermid Printing Solutions, L.L.C. ("MacDermid") has (1) manufactured and sold flexographic printing elements (a) that directly infringe one or more claims of DuPont's United States Patent No. 6,171,758 B1 ("'758 patent"), and (b) to be used, treated, processed, or developed in a manner that directly infringes one or more claims of DuPont's United States Patent No. 6,773,859 B2 ("'859 patent"), and (2) encouraged others to infringe one or more claims of the '758 patent and '859 patent. (Dkt. entry no. 1, Compl. at ¶¶ 6-9, 14-17.) MacDermid counterclaims, seeking a judgment declaring that (1) it does not infringe either patent, and (2) both patents are invalid. (Dkt. entry no. 73, 2d Am. Answer, Affirmative Defenses & Counterclaims at 14-31.)<sup>1</sup>

---

<sup>1</sup> MacDermid commenced a separate action against DuPont, alleging, inter alia, the infringement of MacDermid's United States Patent No. RE39,835. See No. 07-4325 (MLC).

DuPont moved to preliminarily enjoin MacDermid from directly infringing the '859 patent; the Court denied that motion. (Dkt. entry no. 31, Mot. for Prelim. Inj.; dkt. entry no. 193, Order; dkt. entry no. 192, Op. ("Prelim. Inj. Op.")) In doing so, the Court tentatively construed some terms contained in claim 1 of the '859 patent. (Prelim. Inj. Op. at 21-53.) The Court now provides a final construction of several disputed terms from the '859 Patent and '758 patent.

The parties filed briefs and documentation to support their respective proposed constructions.<sup>2</sup> The Court considered those papers and heard oral argument (dkt. entry no. 297, Tr.), and thereby conducted a Markman hearing. See Markman v. Westview Instruments, 52 F.3d 967 (Fed. Cir. 1995), aff'd, 517 U.S. 370 (1996). The Court takes into account a "[Proposed] Consent Order

---

<sup>2</sup> The submissions include: (1) MacDermid's Opening Markman Brief ("MacDermid Opening Brief"), with attached declarations and exhibits (dkt. entry no. 77); (2) DuPont's Opening Claim Construction Brief ("DuPont Opening Brief"), with an attached declaration and exhibits (dkt. entry no. 78); (3) DuPont's Responsive Claim Construction Brief ("DuPont Responsive Brief"), with an attached declaration and exhibits (dkt. entry no. 95); (4) MacDermid's Brief in Opposition to DuPont's Opening Brief ("MacDermid Responsive Brief"), with an attached declaration and exhibits (dkt. entry no. 96); (5) MacDermid's Brief in Reply to DuPont's Responsive Brief ("MacDermid Reply Brief"), with an attached declaration and exhibits (dkt. entry no. 103); (6) an April 30, 2007 letter from DuPont explaining that it would not file a "Reply Claim Construction Brief"; (7) redacted and unredacted versions of MacDermid's Supplemental Claim Construction Memorandum of Law ("MacDermid Supplemental Brief"), with a declaration and exhibits (dkt. entry nos. 223 & 224); and (8) DuPont's Response to MacDermid's Supplemental Claim Construction Brief ("DuPont Supplemental Brief"), with a declaration and an exhibit (dkt. entry no. 231).

on Claim Construction" filed by DuPont for both parties ("Proposed Consent Order"). (Dkt. entry no. 279.) The Court issues the following findings of fact and conclusions of law as to the construction of the claims in the '758 patent and '859 patent.

#### **BACKGROUND**

##### **I. The '758 Patent**

###### **A. The Claims**

The '758 patent is entitled "Dimensionally Stable Flexographic Printing Plates". (Dkt. entry no. 78-1, Decl. of Tricia Bevelock O'Reilly ("O'Reilly Decl."), Ex. B, '758 Patent.) The abstract states that:

The present invention is a flexographic printing plate having a very low degree of thermal distortion during development. This flexographic printing plate comprises a dimensionally stable substrate and an image bearing relief layer, wherein the thermal distortion of the flexographic printing plate in both the machine and the transverse directions is less than 0.02% when the plate is developed at temperatures in the range from about 100°C. to about 180°C.

(Id. at Abstract.) The '758 patent is composed of 21 claims, but only claims 1 and 19 are independent. (Id. at cols. 8-10.) DuPont asserts claims 1, 3, 4, 6, and 8 against MacDermid here. The parties disagree as to the meaning of four terms: in claim 1, (1) "dimensionally stable"; (2) "thermal distortion"; and (3) "developed"; and, in claim 4, (4) "thermoplastic elastomeric block copolymer".

Claim 1 of the '758 patent states:

**1. A photosensitive plate suitable for use as a flexographic printing plate comprising a dimensionally**

stable, flexible, polymeric substrate and a photosensitive elastomer layer, wherein the plate has a thermal distortion in both the machine and the transverse directions which is less than 0.03% when the plate is exposed to actinic radiation and, after exposure, is developed at temperatures between 100 and 180° C.

(Id. at col. 8, lines 18-25.)

In turn, claim 4 covers:

**4.** The plate of claim 1 wherein the photosensitive elastomer layer comprises a thermoplastic elastomeric block copolymer mixed with a cross-linking agent and a photoinitiator.

(Id. at col. 8, lines 31-34.)

#### **B. Prosecution History**

The application leading to the '758 Patent was filed in November 1994. (Id. at Filed.) In an Office Action mailed in March 1995, the United States Patent and Trademark Office ("PTO") examiner found the claims subject to a restriction or election requirement. (Dkt. entry no. 77-2, Decl. of James Mahanna ("Mahanna Decl."), Ex. 10, '758 Patent Prosecution History ("Prosecution History") at 3-1 to 3-5.) After the applicants filed a response in April 1995 (id. at 5-1 to 5-2), the examiner rejected the claims in an Office Action mailed in June 1995. (Id. at 6-1 to 6-10.) The applicants traversed the rejections in a response filed in August 1995. (Id. at 7-1 to 7-9.) The examiner finally rejected the claims in a November 1995 Office Action. (Id. at 8-1 to 8-12.) The applicants submitted an amendment and response in January 1996. (Id. at 9-1 to 9-7.) They then appealed to the

Board of Patent Appeals and Interferences ("Appeals Board").  
(Id. at 11-1.)

The applicants submitted a brief defending the patent claims, which was received in April 1996. (Id. at 12-1 to 12-16.) The examiner also submitted an answer defending the rejections. (Id. at 13-2 to 13-16.) In a decision mailed on June 29, 2000, the Appeals Board disagreed with the examiner and allowed the patent to be issued. (Id. at 18-1 to 18-6.) The '758 patent was issued on January 9, 2001.

## **II. The '859 Patent**

The '859 patent was issued on August 10, 2004; it is entitled "Process For Making A Flexographic Printing Plate And A Photosensitive Element For Use In The Process". (O'Reilly Decl., Ex. A, '859 Patent ("'859 Patent").) The abstract discloses:

The invention relates to a process for preparing a flexographic printing plate from a photosensitive element having a photopolymerizable layer and a thermally removable layer on the photopolymerizable layer. The process includes imagewise exposing the photosensitive element and thermally treating the exposed element to form a relief suitable for use in flexographic printing. The thermally removable layer can be transparent or opaque to actinic radiation. The invention also relates to a photosensitive element for use in this process. The photosensitive element includes a photopolymerizable layer and at least one thermally removable layer having a filler and a binder, wherein the binder is less than 49% by weight, based on the total weight of the binder and filler.

(Id. at Abstract.) The '859 patent is composed of 54 claims, but only claims 1 and 51 are independent. (Id. at cols. 43-48.) DuPont alleges infringement of claims 1(1) (a), 6, 21, 22, 30, 33,

36, 40, 41, and 48. The parties advance different constructions of five terms: in claim 1, (1) "softening or melting temperature"; (2) "filler"; and (3) "particulate material"; and, in claim 21, (4) "release layer"; and (5) "surface modifying layer".

Claim 1 states:

**1.** A process for making a flexographic printing plate comprising:

1) providing a photosensitive element comprising: at least one photopolymerizable layer on a support comprising an elastomeric binder, at least one monomer, and a photoinitiator, and at least one thermally removable layer disposed above the photopolymerizable layer, the thermally removable layer selected from the group consisting of

(a) an actinic radiation opaque layer comprising (i) at least one infrared absorbing material, (ii) a radiation opaque material, wherein (i) and (ii) can be the same or different, and at least one binder having a softening or melting temperature less than 190°C.;

(b) a layer of a composition comprising at least one binder and filler, wherein the binder is less than 49% by weight based on the total weight of the binder and filler, and

(c) a layer of particulate material having particle size of less than 23 micrometers;

2) imagewise exposing the photopolymerizable layer to actinic radiation forming polymerized portions and unpolymerized portions; and

3) thermally treating the element of step 2) by heating to a temperature sufficient to remove the thermally removable layer and to remove the unpolymerized portions of the photopolymerizable layer and form a relief.

(Id. at col. 43, lines 34-40.)

Claim 21 states:

**21.** The process of claim 1 wherein the photosensitive element further comprises at least one more additional layer selected from the group consisting of:

release layer, adhesion-modifying layer, barrier layer, and surface modifying layer, wherein the at

least one more additional layer is transparent to actinic radiation.

(Id. at col. 45, lines 16-21.)

## DISCUSSION

### I. Applicable Legal Standards

The Court, in a patent infringement inquiry, first determines the scope and meaning of the patent claims as a matter of law.

Markman, 52 F.3d at 979. The Court then compares the allegedly infringing device to each claim at issue to determine if "all of the limitations of at least one claim are present, either literally or by substantial equivalent, in the accused device."

Teleflex, Inc. v. Ficosa N. Am. Corp., 299 F.3d 1313, 1323 (Fed. Cir. 2002). The Court is primarily concerned with the first step here.

There is a heavy presumption that a claim term carries its ordinary and customary meaning. CCS Fitness v. Brunswick Corp., 288 F.3d 1359, 1366 (Fed. Cir. 2002). The ordinary and customary meaning of a claim term is the meaning that a "person of ordinary skill in the art in question" would give such a term on the effective filing date of the patent application. Phillips v. AWH Corp., 415 F.3d 1303, 1313 (Fed. Cir. 2005). Such a person is deemed to interpret the claim term in the context of the entire patent, including the specification and prosecution history. Id. Thus, the words in a claim are generally given their ordinary and customary meaning in the absence of a contrary indication in the

patent specification or file history. Wolverine World Wide v. Nike, Inc., 38 F.3d 1192, 1196 (Fed. Cir. 1994).

When interpreting an asserted patent claim, the Court looks first to the intrinsic evidence of record, which includes the patent's claims, specification, and complete prosecution history. Such intrinsic evidence is the most significant source for the legally operative meaning of disputed claim language. Vitronics Corp. v. Conceptronic, Inc., 90 F.3d 1576, 1583 (Fed. Cir. 1996). In reviewing the intrinsic evidence, the Court considers the context in which a term is used within both the claim at issue and the claims not at issue. Phillips, 415 F.3d at 1314. The same term appearing in different claims should generally be given the same meaning unless it is clear from the specification and prosecution history that the term at issue has a different meaning from claim to claim. Fin Control Sys. Pty v. OAM, Inc., 265 F.3d 1311, 1318 (Fed. Cir. 2001). Similarly, differences between claims can be useful in arriving at the proper construction. Phillips, 415 F.3d at 1314. Under the doctrine of claim differentiation, the presence of a dependent claim adding a further limitation raises a presumption that the same limitation is not present in the independent claim. Phillips, 415 F.3d at 1315; RF Del. v. Pac. Keystone Techs., 326 F.3d 1255, 1263 (Fed. Cir. 2003). But such a presumption may be trumped by a clear and unambiguous disclaimer. Seachange Int'l v. C-COR Inc., 413 F.3d 1361, 1369 (Fed. Cir. 2005).

The specification is always highly relevant to the claim construction analysis, and is the single best guide to the meaning of a disputed term. Honeywell Int'l v. ITT Indus., 452 F.3d 1312, 1318 (Fed. Cir. 2006). The specification may contain an intentional disclaimer or a disavowal of claim scope by the inventor, in which case the inventor's intention, expressed in the specification, is dispositive. Phillips, 415 F.3d at 1316. But it is improper to read a limitation from the specification into the claims themselves. Teleflex, 299 F.3d at 1326. Therefore, the Court should "not import limitations from a preferred embodiment" described in the specification. Seachange Int'l, 413 F.3d at 1377.

The prosecution history shows (1) how the inventor understood the patent, and (2) whether the inventor limited the invention during the course of the patent prosecution, thus narrowing the scope of the ultimately patented product. Phillips, 415 F.3d at 1317. As the prosecution history reflects ongoing negotiations between the inventor and the PTO, it is often less clear and less useful than the specification. Id.

The Court may in certain circumstances consider "extrinsic evidence", including "expert and inventor testimony, dictionaries, and learned treatises." Phillips, 415 F.3d at 1317. In general, such evidence is less reliable than its intrinsic counterparts. Id. at 1318. In some situations, the ordinary meaning of claim language as understood by a person of skill in the art will be

readily apparent, and claim construction will then involve the simple application of the widely accepted meanings of commonly understood words. Id. at 1314. In such circumstances, general purpose dictionaries may be helpful. Id. However, "heavy reliance on the dictionary divorced from the intrinsic evidence risks transforming the meaning of the claim term to the artisan into the meaning of the term in the abstract, out of its particular context, which is the specification." Id. at 1321. Also, expert evidence may be useful for certain limited purposes. Id. at 1318. However, unsupported assertions by experts as to the definition of a claim term are not useful, and the after-the-fact testimony of the inventor is accorded little if any weight in the claim construction inquiry. Id.; Bell & Howell Document Mgmt Prods. Co. v. Altek Sys., 132 F.3d 701, 706 (Fed. Cir. 1997).

If, after applying these principles, the Court concludes that a claim term remains "insolubly ambiguous", it must hold that the claim limitation is indefinite. Honeywell v. Int'l Trade Comm'n, 341 F.3d 1332, 1340-42 (Fed. Cir. 2003). When that occurs, the Court must strike down all claims of which the term is a part as indefinite and therefore invalid pursuant to 35 U.S.C. § 112. Aero Prods. Int'l v. Intex Recreation, 466 F.3d 1000, 1005 (Fed. Cir. 2006).

## **II. Legal Standards Applied Here**

The parties have reduced the number of terms in dispute to nine, specifically four terms in the '758 patent and five terms

in the '859 patent. The Court therefore only addresses these remaining disputed terms here. It is noted that the parties have submitted a Proposed Consent Order as to a number of terms no longer in dispute, which the Court will enter along with this Opinion and Order

**A. Construction of the '758 Patent**

**1. Claim 1**

**a. "dimensionally stable"**

DuPont proposes this construction of the term "dimensionally stable": "a polymeric substrate that results in a flexographic printing plate having thermal distortion of less than 0.03% when developed at temperatures between 100 and 180°C, or [results in] an individual polymeric substrate having less than 0.07% distortion when heated to temperatures from 110 to 180°C". (DuPont Opening Br. at 21.) The first component of this proposed construction deals with the meaning of the term "dimensionally stable" as used in claim 1. ('758 Patent at col. 8, lines 18-25.) The second component addresses the use of this term in claim 19. (Id. at col. 10, lines 1-6.)

MacDermid proposes this construction, which it actually modified over the course of the claim construction proceedings:

A flexible polymeric substrate whose dimensional stability has been controlled through a special annealing process, namely an annealing process that: (1) is in addition and subsequent to the heat treating steps associated with manufacturing the polymeric film, (2) is not the process of bonding the photosensitive elastomer layer to the polymeric substrate, and (3) comprises: (i) heating the substrate to a temperature above its glass

transition temperature but below its melting temperature and at or greater than the temperature to which the substrate is later subjected during thermal development, (ii) at tensions of less than 200 psi, and (iii) for a time greater than the time required to bring the film to the annealing temperature, such that a specially annealed substrate has less thermally induced distortion than a non-specially annealed substrate.

(MacDermid Supplemental Br. at 3-4.) The parties devoted much attention to this term in their briefing, with the supplemental briefing exclusively concerned with the proper construction of this term, and at the Markman hearing. They raise a range of complicated issues, but the heart of the dispute appears to be over whether the claim term at issue here should be construed as limited to a so-called "special annealing process."

DuPont argues that: (1) its own construction is supported by (a) the plain language of claim 1, which defines "dimensionally stable" by reference to the thermal distortion limit of 0.03%, and (b) the specification, which also indicates that the term should be defined by reference to the thermal distortion limit and otherwise states that "[t]he present invention is a flexographic printing plate having a very low degree of thermal distortion during development" ('758 Patent at col. 1, lines 51-53); (2) MacDermid's proposed construction improperly imports process limitations from the specification into a product claim and otherwise improperly limits the claim to a preferred embodiment; (3) the specification lacks the clear disavowal required to adopt MacDermid's proposed construction; (4) the term "special annealing

process" is not used in the claims; (5) the specification only mentions the term "special annealing process" once, in the context of discussing a preferred embodiment using semicrystalline polymers; (6) such semicrystalline polymers are actually claimed in dependent claim 7, and, under the doctrine of claim differentiation, this embodiment should not be read into the broader claim 1; (7) because of the examiner's determination that the applicants had to choose between the product and the process claims, the applicants actually cancelled claim 23, which claimed a method of making a flexible photosensitive element by "annealing a semi-crystalline polymeric firm at temperatures of at least 120°C and tensions less than  $1.4 \times 10^6$  N/m<sup>2</sup>" and "by coating onto the annealed polymeric film a photopolymerizable composition" (Prosecution History at 1-21 (emphasis added)); (8) to overcome the examiner's inherency rejection, the applicants merely had to demonstrate one example of a plate made with the same substrate that did not achieve the claimed thermal distortion, and such a demonstration did not amount to the requisite clear disavowal of claim scope; (9) the prosecution history otherwise lacks any such disavowals; (10) MacDermid's requirement in subsection (1) of its proposed construction that the annealing process be in addition and subsequent to the heat treating steps associated with manufacturing the film is not found in the claims themselves; (11) MacDermid's additional requirements, found in subsections

(2) and (3) of its proposed construction, also are not found in either the claims, the specification, or the prosecution history; and (12) these additional steps are actually covered in dependent claims 9 and 16 and therefore it would be inappropriate to read them into claim 1 given the claim differentiation doctrine.

(DuPont Opening Br. at 17-20; DuPont Responsive Br. at 2-12; DuPont Supplemental Br. at 1-20; Tr. at 69-84, 186-94.)

MacDermid, in contrast, argues that: (1) DuPont's proposed construction ignores the requirement of a special, further, and important annealing step, which was used by the applicants to secure the issuance of the '758 patent; (2) DuPont's proposed construction collapses the term "dimensionally stable" into the term "thermal distortion", thereby effectively eliminating the "dimensionally stable" limitation from the claim itself; (3) DuPont's approach improperly grants it a right to exclude as to all thermally developed plates with favorable thermal distortion regardless of how this distortion result is achieved and even though the patent itself describes only one means to achieve this result; (4) the specification supports MacDermid's proposed construction because it: (a) describes the problem of thermal distortion, (b) states that a "special annealing process" solves this problem, (c) identifies the "special annealing process" as comprised of the three parameters of temperature, tension, and time, (d) discusses these three parameters in some detail, (e)

notes that various annealing methods exist, such as air-oven annealing, hot can annealing, or combinations of such methods, and (f) provides four examples wherein the annealed samples are compared to non-annealed samples; (5) the prosecution history further supports its proposed construction because – to overcome the examiner's rejections, distinguish prior art, and prevail on appeal – the applicants repeatedly relied upon the "special annealing process", and the Appeals Board cited their annealing arguments to reverse the examiner's rejections; (6) the extrinsic evidence, including the deposition testimony of an inventor, supports the "special annealing process" construction; and (7) as a matter of law, (a) the applicants intentionally and clearly disclaimed or disavowed the claim scope and otherwise disparaged non-annealed substrates and photosensitive plates made with non-annealed substrates, (b) the claims must be construed in light of the prosecution history, as the applicants successfully argued that their claims were enabled and distinguished from prior art due to the "special annealing process", (c) the extrinsic evidence, although less significant than the intrinsic evidence, should be viewed as supporting the proposed construction, (d) MacDermid's proposed construction does not improperly import limitations from a preferred embodiment, as it relies on the specification's identification of the "special annealing process" as the inventors' "discovery", and (e) the "special annealing

process" should be treated as part of the product claims because the process steps form an essential part of the invention. (MacDermid Opening Br. at 8-20; MacDermid Responsive Br. at 15-25; MacDermid Reply Br. at 1-8; MacDermid Supplemental Br. at 1-29; Tr. at 92-142.)

Both parties have presented reasonable – if complicated – arguments for the Court to consider. But the Court agrees with MacDermid's proposed construction, in view of the specification and the prosecution history of the '758 patent itself.

As MacDermid explains, the patent specification repeatedly highlights the importance of annealing. The specification even states that "[t]he desirability of such semicrystalline polymers arises from the discovery that dimensional stability of these polymer substrates may be controlled through a special annealing process." ('758 Patent at col. 2, lines 55-59.) In addition to mentioning different annealing methods, the specification explains this annealing process, focusing on temperature, tension, and time. (Id. at col. 2, lines 59-67, col. 3, lines 1-26.) The specification then provides four examples, in which the crucial distinguishing feature of the testing was whether the tested samples were in fact subjected to annealing. (Id. at col. 5, lines 26-66, col. 6, lines 1-67, col. 7, lines 1-67, col. 8, lines 1-16.) In turn, the applicants significantly found that the annealed samples showed less thermal distortion than their non-annealed counterparts. (Id.)

The prosecution history also supports MacDermid's proposed construction. In overcoming the examiner's rejections, the applicants repeatedly emphasized the whole notion of annealing. Indeed, in their August 1995 response, the applicants responded to the examiner's 35 U.S.C. § 103 obviousness rejection by stating:

The concept that all flexographic printing plates, including those disclosed in Martens and Prioleau, will have some "inherent" degree of thermal distortion, does not overcome Martens' and Prioleau's lack of teaching or suggestion as to the importance or desirability of dimensional stability. There is no basis for the inference that the inherent degree of distortion in Martens' and Prioleau's plates is in the range claimed. In fact, the Examples in the specification show that absent a critical annealing step, many polymeric films, including PEN and PET films, and plates made from such films do not meet the low distortion levels claimed in the present invention.

(Prosecution History at 7-5 (emphasis added).) As to the 35 U.S.C. § 112 enablement rejection, the applicants argued "that Examples 3 and 4 additionally provide support and enablement for the invention as described in Claim 1." (Id. at 7-3.) In their subsequent January 1996 response, the applicants defended their claims against an anticipation rejection under 35 U.S.C. § 102 by asserting:

The rejection indicates that, nevertheless, Martens or Prioleau anticipate the present claims because they disclose substrate materials, e.g., polyethylene terephthalate, which the Examiner asserts "inherently have the characteristic of experiencing" low thermal distortion. There is no basis for the assertion that Martens' and Prioleau's plates or substrates inherently possess the degree of distortion in the range claimed. In fact, the Examples in the specification show that absent further treatment by annealing, many polymeric films, including polyethylene naphthalate and

polyethethelene terephthalate films, and plates made from such films do not meet the low distortion levels claimed in the present invention. Example 4, which discusses plates made with polyethethelene terephthalate substrates, clearly demonstrates that not all polyethylene terephthalate films will yield plates having the claimed maximum distortion levels. The other examples show similar findings for polyethylene naphthalate films. Therefore, the specification clearly rebuts the assertion that polyethylene terephthalate films and plates made from such inherently have the characteristic of low thermal distortion as required by the claims. In view of the clear evidence set forth in the specification, Applicants respectfully assert that this rejection under 35 U.S.C. 102(b) is improper and should be withdrawn.

(Id. at 9-3 to 9-4 (emphasis added).) Responding to the obviousness rejection, the applicants again emphasized the importance of the annealing process:

The Martens patents and Prioleau are addressed to photosensitive plates and flexographic printing plates made therefrom having specific chemistry and construction. These patents do disclose that the plates can have polymeric substrates. The Examiner acknowledges that these references do not teach the important annealing step which enables one to achieve the very low degrees of distortion. Locey teaches a specific method of heat treating film to avoid draw lines which are out-of-plane distortions of biaxially oriented film. Lu teaches an alternate method of providing films that have thermal distortions less than 0.5%. However, Lu does not contain any specific showing that distortions of 0.07% or less can be obtained.

(Id. at 9-5 (emphasis added).)

The brief filed by the applicants with the Appeals Board contained even more pointed references to the "special annealing process." At the end of the "Summary of the Invention" section, the applicants stated:

Applicants have achieved such reduced levels of thermal distortion by subjecting the substrate of the plate to

a special annealing process. This process is described at page 4, line 15 through page 6, line 190 of the specification.

(Id. at 12-6 (emphasis added).) They then reiterated many of the same arguments they had previously made to the examiner. Dealing with the anticipation rejection, the applicants stated that "the examples in the specification of the present invention show that absent further treatment by annealing, many polymeric films (including polyethylene naphthalate and polyethylene terephthalate films) and plates made from such films do not meet the low distortion levels claimed in the present invention." (Id. at 12-9 (emphasis added).) The applicants discussed the four examples, noting the different thermal distortion results obtained based on whether the samples had been annealed. (Id.) As to the issue of obviousness, the applicants emphasized that "[t]he Examiner acknowledges that these references do not teach the important annealing step which enables one to achieve the very low degrees of thermal distortion." (Id. at 12-11 (emphasis added).)

The applicants' contentions were successful, and the Appeals Board allowed the patent to be issued. The Appeals Board even relied on the annealing arguments in its June 29, 2000 decision, stating that:

Each of the § 102 rejections before us on this appeal is based upon the examiner's proposition that the respective plates of the applied references inherently possess limited distortion within the here claimed ranges because the prior art and here claimed plates may be manufactured from the same polymeric material,

namely, polyethylene terephthalate. The appellants point out, however, that polyethylene terephthalate printing plates which are not annealed in accordance with their disclosed invention (i.e., the plates of Martens, Gibson or Worns) do not necessarily and inherently possess distortion values within the appealed claim ranges as evidenced by Example 4 including Table IV on pages 13 and 14 of the subject specification. Significantly, the examiner has not responded meaningfully to the appellants' point on this matter.

. . . . Under the circumstances recounted above, it is clear that the record before us on this appeal reflects that polyethylene terephthalate printing plates which have not been subjected to the annealing process disclosed by the appellants, that is, the plates of the references under consideration, do not necessarily and inherently possess the appellants' claimed distortion values.

(Id. at 18-3 to 18-4 (emphasis added).) The Appeals Board then "perceive[d] substantial merit in the appellants' arguments against the examiner's conclusion of obviousness." (Id. at 18-4.)

The Court thus construes the term "dimensionally stable" in light of the clear and unambiguous statements regarding the annealing process made in both the specification and over the course of the prosecution history. Cf., e.g., Novo Nordisk A/S v. Sanofi-Aventis U.S., No. 07-3206, 2009 WL 2185905, at \*8 (D.N.J. July 22, 2009) ("The Court concludes that the specification and the prosecution history do not include expressions of manifest exclusion or restriction, representing a clear disavowal of claim scope, that demonstrate an intent to limit the invention to devices that have a gearbox and a non-rotatable piston rod" (citing Teleflex, 299 F.3d at 1327-28)). The Court therefore adopts the construction proposed by MacDermid.

**b. "thermal distortion"**

DuPont asks the Court to construe the term "thermal distortion" as meaning "[t]he magnitude of change in the machine and transverse direction caused by thermal development of the flexographic printing plate." (DuPont Responsive Br. at 13.) But MacDermid advances the following construction of this term: "The magnitude of plate image distortion in the machine and transverse direction caused by thermal development of the flexographic printing plate that is measured by comparing the developed image of the flexographic printing plate with the image of the negative phototool." (MacDermid Opening Br. at 20.)

DuPont contends that its proposed construction should be adopted because it is: (1) supported by the plain language of claim 1 itself, which refers to thermal distortion "in both the machine and the transverse directions" ('758 Patent at col. 8, lines 21-22); (2) consistent with the specification, which states that the "[t]he thermal distortion (includes both elongation and shrinkage) of the plate in both the machine and the transverse directions is less than 0.03%" (id. at col. 2, lines 22-24) and (in Example 1) that "[t]he amount of distortion was well balanced between the machine and transverse directions" (id. at col. 5, lines 44-46); and (3) "[s]imple and straightforward" (Tr. at 84). (DuPont Responsive Br. at 12; Tr. at 84-88.)

As to MacDermid's proposed construction, DuPont argues that: (1) the '758 patent and its prosecution history are not limited to

phototools or analog printing plates; (2) although the '758 patent contains no express "digital" references, "[i]t is well settled law that the '758 patent does not have to expressly describe embodiments directed to digitally imaged flexographic printing plates for the claims to be construed to cover digitally imaged plates" (DuPont Responsive Br. at 14 (citations omitted)); and (3) the proposed construction would require use of a single measuring technique even though the specification provides several examples of how to measure thermal distortion. (DuPont Responsive Br. at 13-14; Tr. at 84-88.)

DuPont counters MacDermid's assertions that DuPont's proposed construction would render the '758 patent insolubly ambiguous and indefinite by arguing that: (1) "[t]hermal distortion of an analog plate, a digitally imaged plate or the individual polymeric substrate are all easily measured by comparing the dimensions of the plate or substrate before and after being developed with heat" (DuPont Responsive Br. at 15); (2) in contrast to the infringer in Honeywell v. International Trade Commission, 341 F.3d 1332 (Fed. Cir. 2003), "MacDermid can only point to the arguments of its attorneys, not credible factual evidence, to support its contention that the particular method used to determine thermal distortion is 'critical' to determining thermal distortion" (DuPont Responsive Br. at 16); and (3) the patent does not have to describe a specific and exclusive measurement technique, as a

person of ordinary skill in the art would know how to conduct the proper measurement and, at a trial, the parties' experts will explain how they measured the distortion. (Id. at 15-16; Tr. at 182-86.)

MacDermid defends its proffered construction on the grounds that: (1) the specification "only describes analog plates, analog imaging, and a measurement technique for thermal distortion of analog imaged plates" (MacDermid Opening Br. at 21); (2) the measurement of thermal distortion of the plate is only described in Examples 3 and 4 of the specification, and, in both instances, the method measures the developed image against the image on the "negative" ('758 Patent at col. 7, lines 16, 58-59); (3) the measurement technique identified in Examples 3 and 4 in the specification cannot be used with digitally imaged plates because "the in situ mask is thermally processed (and destroyed) during development" (MacDermid Opening Br. at 22); (4) the prosecution history confirms that the exclusive method of measuring thermal distortion is found in Examples 3 and 4, with the applicants stating "that Examples 3 and 4 additionally provide support and enablement for the invention as described in Claim 1" to overcome the examiner's enablement rejection (Prosecution History at 7-3); and (5) any construction of "thermal distortion" to include digital flexographic plates would render the claims invalid for failure to meet the enablement requirement and invalidate the claims of

the subsequent '859 patent on anticipation grounds. (MacDermid Opening Br. at 20-23; MacDermid Reply Br. at 9-10; Tr. at 142-54.)

MacDermid also argues that DuPont's proposed construction of "thermal distortion" must be rejected because it would "render the claim limitation 'insolubly ambiguous' and indefinite." (MacDermid Opening Br. at 23.) Specifically, it contends that:

First, as noted, the '758 specification fails to describe any measurement technique of "thermal distortion" of a printing plate other than comparing the imaged surface to the analog phototool. Second, one could conceive of innumerable measurement techniques for "thermal distortion" of an imaged plate. Third, and most significant to the Court's evaluation of indefiniteness, these measurement techniques can result in varied and disparate results.

(Id. at 24.) According to MacDermid, the Court confronts a situation similar to the one addressed in Honeywell:

[T]here are two possible constructions of "thermal distortion" - the first is an "any one method" and the second is an "all methods." No guidance is given to the Court (or the public) as to which construction is correct, particularly, in the context of a digitally imaged plate. Moreover, different and potentially contradictory results are reached depending on the measurement method employed and/or the equipment used.

(Id. at 25-26.) MacDermid also contends that Examples 1 and 2 of the '758 patent, cited by DuPont, provide two methods to measure the thermal distortion of the substrate, but that claim 1 is concerned with the thermal distortion of the plate while claim 19 expressly addresses the "distortion" in the "said polymeric substrate" ('758 Patent at col. 10, lines 4-5). (Tr. at 142-52.) MacDermid asserts that DuPont's proposed construction fails to define what should be measured and how it should be measured, and

that DuPont improperly leaves it up to a jury to decide which measurement methodology is correct and thereby usurps the Court's responsibility of defining the scope of a patent claim. (Id.)

The parties present the Court with a difficult choice with their contentions. But the Court agrees with DuPont's arguments and adopts its simple and common-sense construction, which also has substantial support in the intrinsic evidence. It would be inappropriate to strike down this construction as indefinite, at least at this juncture. Thus, "thermal distortion" is construed to mean "the magnitude of change in the machine and transverse direction caused by thermal development of the flexographic printing plate."

**c. "developed"**

DuPont asserts that the term "developed" should be construed to mean "[t]reated to form a flexographic printing plate." (DuPont Responsive Br. at 18.) But MacDermid defines the term as the "[r]emoval of unexposed, uncured portions of the photosensitive elastomer layer." (MacDermid Opening Br. at 32.)

DuPont argues that its proposed construction is supported by (1) the word's commonly accepted definition, and (2) the intrinsic evidence and context of the '758 patent, which is directed to a photosensitive element that can be thermally developed to form a flexographic printing plate. (DuPont Responsive Br. at 18-19; Tr. at 89-92.) It also attacks MacDermid's proposed construction as

too narrow because it does not cover the removal of other layers such as the in situ mask. (Tr. at 89-92.) MacDermid contends that its approach is supported by language contained in the patent's specification. (MacDermid Opening Br. at 32; Tr. at 154-56.) MacDermid further attacks DuPont's alternative construction as too broad and unduly ambiguous. (Tr. at 154-56.)

The Court agrees with MacDermid. The specification for the '758 patent defines "developed" by stating: (1) "In a thermal development process, the photosensitive layer, which has been image-wise exposed to actinic radiation, is contacted with an absorbent layer at a temperature sufficient to cause the composition in the unexposed portions of the photosensitive layer to soften or melt and flow into the absorbent material" ('758 Patent at col. 1, lines 41-46); and (2) "'Developing temperature' is the temperature to which the imagewise exposed photosensitive layer is heated to remove the uncured portions of the layer" (id. at col. 2, lines 5-7). The Court therefore construes "developed" as meaning the "removal of unexposed, uncured portions of the photosensitive elastomer layer."

## 2. **Claim 4, "thermoplastic elastomeric block copolymer"**

The parties did not address the proper construction of "thermoplastic elastomeric block copolymer" at the hearing, as they hoped to arrive at an agreement on this term. (10-27-09 Letter at 1.) They have not done so, and now ask the Court to construe the term after considering their respective briefs.

(Id.) According to DuPont, the Court should construe the term to mean: "A class of polymeric materials composed of two or more comonomeric units in extended segments having hard and soft blocks." (DuPont Responsive Br. at 19-20.) MacDermid offers the following construction: "Any one of a class of elastic polymers containing long stretches of two or more monomeric units linked together by chemical valences in one signal chain that become soft when heated and returns to its original condition when cooled." (MacDermid Opening Br. at 32.)

DuPont asks the Court to adopt its proposed construction, as:

(1) the patent's specification provides examples of acceptable "thermoplastic elastomeric block copolymers" ('758 Patent at col. 4, lines 13-26); (2) the specification also states that: "The elastomeric block copolymer is preferably an A-B-A- type block copolymer, where A is a nonelastomeric block, preferably a vinyl polymer and most preferably polystyrene and B is an elastomeric block, preferably polybutadiene or polyisoprene. The nonelastomer to elastomer ratio is preferably in the range of from 10:90 to 35:65" (id. at col. 4, lines 15-21); (3) "even though the patent does not expressly provide a definition of this phrase, it is readily understood by those of ordinary skill in the art in the context of '758 patent" (DuPont Responsive Br. at 20 (citing dictionary definitions)); and (4) the construction proposed by MacDermid is not consistent with the intrinsic evidence and is improperly cobbled together from separate dictionary definitions

of "thermoplastic", "elastomer", and "block co-polymer". (DuPont Responsive Br. at 19-20.) MacDermid contends that its proposed construction should be adopted because: (1) the "non-limited list of preferred substances" provided in the specification "is not a proper construction as the Federal Circuit has held numerous times that one cannot limit a construction to only those preferred embodiments found in the specification" (MacDermid Opening Br. at 33 (citation omitted)); and (2) its proposed construction of this term, which is "common in the field of flexography", is supported by Hawley's Condensed Chemical Dictionary's definitions of "thermoplastic," "elastomer," and "block co-polymer" (*id.* at 33 (citing definitions)).

The Court, upon considering the parties' respective arguments and the intrinsic and extrinsic evidence, agrees with DuPont. Accordingly, the term "thermoplastic elastomeric block copolymer" is construed to mean "a class of polymeric materials composed of two or more comonomeric units in extended segments having hard and soft blocks."

#### **B. Construction of the '859 Patent**

##### **1. Claim 1**

###### **a. "softening or melting temperature"**

The Court tentatively construed the term "softening or melting temperature" in its Preliminary Injunction Opinion "as referring to any temperature at which the viscosity of the binder contained in the photopolymerizable layer will be reduced to such

a point that the thermally removable layer, or portions thereof, may be removed by absorbing material." (Prelim. Inj. Op. at 44-45.) The Court, in reaching this conclusion, expressly considered and rejected MacDermid's contention that the term itself is indefinite. (Id. at 42-45.)

At the subsequent Markman hearing, MacDermid attacked the tentative construction and asserted that the term at issue is irreparably indefinite. (Tr. at 157-71.) Evidently accepting the validity of the melting temperature component, it contends that "we have a critically fatal indefiniteness problem with respect to the softening part." (Id. at 157.) MacDermid argues:

We believe that the binder in this part of the claim needs to be directed to the binder of the thermally removable layer[,] not the photopolymerizable layer. Secondly, we don't believe that it can be any temperature. It needs to be a particular temperature in order to be definite. And then third, and I think probably most important is Your Honor's construction is functional. It doesn't define the class of binders by what they are. It defines them by how they operate in this particular process, and, therefore, they're functional.

(Id. at 158.) MacDermid contends that the specification (1) does not define the notion of "softening temperature", leaving no way to know exactly what softening is, when it happens, and how to measure it, and (2) creates further uncertainty by "say[ing] some of the above materials do not have an actual softening or melting point." (Id. at 159-60.) As to the extrinsic evidence, MacDermid notes that "softening temperature" is defined as "the temperature at which material transforms a specific amount when measured under

specific examination conditions, i.e., depends on how you measure it and under what circumstances you measure it." (Id. at 160.) Citing Halliburton Energy Services v. M-I LLC, 514 F.3d 1244 (Fed. Cir. 2008), Datamize, LLC v. Plumtree Software, 417 F.3d 1342 (Fed. Cir. 2005), and Honeywell Int'l v. Int'l Trade Comm'n, 341 F.3d 1332 (Fed. Cir. 2003), MacDermid argues that (1) the term is indefinite, (2) the applicant could have adopted an "ISO-known standard", or another objective method or standard, to measure softening, and (3) the Court's functional approach thus does not provide a meaningfully definite boundary because external circumstances affect the softening of different materials, thereby causing the boundary to shift impermissibly. (Id. at 161-67; see Mahanna Decl. Exs. 4-5.)

DuPont defends the Court's tentative construction, with some minor modifications. (Tr. at 44-47, 179-82.) It proposes the following construction: "Any temperature at which the viscosity of the binder will be reduced to such a point that the thermally removable layer, or portions thereof, may be removed." (Tr. at 44 (referring to slide).) It suggests the removal of the statement that the binder is contained in the photopolymerizable layer because "the binder is actually in the actinic radiation opaque layer." (Id. at 45.) It then recommends the removal of the phrase "by absorbing material" because such a process is addressed in claim 36. (Id.) As to MacDermid's assertions of indefiniteness, DuPont argues that MacDermid's position is

inconsistent with language contained in the specification and its own expert's declaration. (Id. at 46-47.) DuPont explains that:

[T]heir expert had no problem construing it. Their expert said, "It's the temperature at which the material becomes inviscid enough to flow, and the purpose of specifying a softening temperature or melting temperature is to insure the flow and, therefore, thermal development -" he's talking about this patent "- can occur at a reasonable processing and developing temperature."

(Id. at 46 (quoting D.I. 44-6 at 6-7).)

MacDermid's contentions are reasonable, but the Court is not persuaded to find the term "softening or melting temperature" indefinite. The Court continues to adhere to the finding in the Preliminary Injunction Opinion that "the intrinsic evidence, including the specification and the context in which the term is used in limitation 1(a) of claim 1, provides a sufficient basis for construing 'softening or melting temperature.'" (Prelim. Inj. Op. at 44 (quoting Phillips, 415 F.3d at 1314-15).) After summarizing MacDermid's indefiniteness assertions, the Court explained:

The specification contains the following statements, which reference the "softening" or "melting" of the thermally removal layer:

Thermally treating the element includes heating the exposed photopolymerizable layer and the thermally removable layer at a temperature sufficient to cause the unexposed (uncured) portions of the element to soften or melt or flow, and contacting the layer to an absorbent surface to absorb the melt or flow portions. The polymerized areas of the photopolymerizable layer have a higher melting temperature than the unpolymerized areas and therefore do not melt, soften, or flow at the development temperatures. The term "melt" is used to describe the behavior of the

unirradiated portions of the photopolymerizable elastomeric layer subjected to an elevated temperature that softens and reduces the viscosity to permit flow and absorption by the absorbent material. (Taylor Decl., Ex. 1, '859 patent, at col. 20, lines 47-60.)

[S]o the process functions to absorb the heated composition layer at any temperature above some threshold for absorption in the absorbent material. A wide temperature range may be utilized to "melt" the composition layer for the purposes of this invention. (Id. at col. 20, lines 63-67.)

The photopolymerizable layer and the thermally removable layer/s are heated by conduction, convection, radiation, or other heating methods to a temperature sufficient to effect melting of the uncured portions but not so high as to effect distortion of the cured portions of the layer. The photosensitive element is heated to a surface temperature above about 40°C.; preferably from about 40°C. to about 230°C. (104-446°F.), more preferably from about 100 to 200°C., and most preferably from 100 to 160°C. in order to effect melting or flowing of the uncured portions of the photopolymerizable layer and the thermally removable layer. The absorbent material contacts the surface of the heated photosensitive element, and absorbs the softened or molten or flowing portions of the elastomeric layer from the unirradiated portions, forming a flexographic printing plate in which the uncured portions are removed to form a relief pattern or surface. The thermally removable layer disposed above the photopolymerizable layer may soften or melt or flow and be absorbed as well by the absorbent material. (Id. at col. 21, lines 8-27.)

Thus, there are multiple references in the specification establishing that the "softening or melting temperature" refers only to the temperature necessary to sufficiently reduce the viscosity of the binder contained in the thermally removable layer so that such layer may be absorbed by the absorbent material.

(Id. at 43-44.) This reasoning, made in the context of the Preliminary Injunction Opinion, is re-affirmed and adopted for

claim construction purposes. But the Court accepts the seemingly minor and evidently uncontested changes suggested by DuPont. Accordingly, "softening or melting temperature" means "any temperature at which the viscosity of the binder will be reduced to such a point that the thermally removable layer, or portions thereof, may be removed."

**b. "filler"**

MacDermid argues that the term "filler" should be defined as referring to: "An inert material consisting of fine particles. The filler may be colorless and transparent or have color and be nontransparent." (MacDermid Opening Br. at 40.) DuPont does not respond to MacDermid's proposed construction in its briefing. The Court, in the Preliminary Injunction Opinion, assumed "that DuPont accept[ed] MacDermid's proposed construction of those terms or phrases that DuPont did not address in its brief." (Prelim. Inj. Op. at 22 n.5.)

DuPont contended at the Markman hearing that there is no need for the term to be construed because it (1) does not assert the specific Markush member containing this term, and (2) would be readily understood by a person of ordinary skill in the art. (Tr. at 47-50.) It further argues that MacDermid's proposed construction improperly reads examples from the specification into the claim. (Id. at 48.) But MacDermid contends that its proposed construction is supported by: (1) Hawley's definition

of the term as an inert mineral powder used in plastic products and rubber mix; (2) the specification's statement that the filler is a fine powder that may have color or be colorless; and (3) the specification's subsequent statement that a colorless particulate matter forms a transparent layer while a particulate matter having color forms a nontransparent layer. (MacDermid Opening Br. at 40-41; Tr. at 175-77.) MacDermid further contends that the term must be construed because invalidity of one member of a Markush group invalidates the entire group. (Tr. at 175-77.)

The Court finds that the term "filler" need not be construed, at least at this point. At the very least, such a term would be readily understood by a person of ordinary skill. Also, the parties evidently agree that the term encompasses inert materials, with DuPont noting that the various "filler" examples provided in the specification are all inert materials. (Tr. at 48.)

**c. "particulate material"**

The term "particulate material" presents the same set of circumstances as the term "filler." MacDermid proffers this construction: "A fine powder. The particulate matter may be colorless and transparent or have color and be nontransparent." (MacDermid Opening Br. at 41.) Yet again, DuPont contended for the first time at the Markman hearing that no construction is necessary because it does not assert the specific Markush member containing this term and because the term "particulate material"

would be readily understood by a person of ordinary skill in the art. (Tr. at 48-50.) DuPont also attacks the proffered construction as improperly reading specification examples regarding color and transparency into the term's definition. (Id.) MacDermid asserts that this term must be construed in order to assess the validity of the overall Markush claim and that its own proposed construction is mandated by the specification itself. (MacDermid Opening Br. at 41; Tr. at 175-77.)

The Court reaches the same conclusion as to "particulate material" that it does with respect to the proper construction of the term "filler": there is no need for a construction at this point. The Court also notes that the parties themselves appear to concur that the specification explicitly defines "particulate material" as a "fine powder." ('859 Patent at col. 14, lines 3-4; MacDermid Opening Br. at 41; Tr. at 50.)

## **2. Claim 21**

### **a. "release layer"**

DuPont asks the Court to construe the term "release layer" as meaning "[a] transparent or substantially transparent layer to actinic radiation," or, as corrected for grammar, "a layer that is transparent or substantially transparent to actinic radiation." (DuPont Responsive Br. at 37.) But MacDermid proposes this construction: "A layer used for ease in placing and removing an image bearing transparency onto and from the photopolymerizable

surface after exposure to a vacuum frame by providing a substantially non-tacky surface to the typically tacky surface of the photopolymerizable layer." (MacDermid Opening Br. at 43.)

Both parties cite the '859 patent specification as support for their respective positions. (DuPont Opening Br. at 37; MacDermid Opening Br. at 43; Tr. at 53-58, 62-65, 171-75, 179.) According to DuPont, MacDermid's proposed construction incorrectly limits the use of a release layer to analog imaging and ignores that, as recognized by both the specification and the Court, such a layer could be used in digital imaging. (Tr. at 53-58, 62-65, 179.) It further contends that MacDermid's proposed construction improperly restricts the term to a preferred embodiment and reads functional limitations into a structural claim element. (DuPont Opening Br. at 37; Tr. at 53-58, 62-65, 179.) MacDermid attacks DuPont's proposed construction as overly broad and inconsistent with the explicit patent language, and adds that a release layer would serve little if any real function in the digital imaging context. (Tr. at 171-75.)

The Court turns to the specification – which provides a lengthy discussion of "release layer" – to construe this term:

The primary purposes of a release layer are for ease in placing and removing an image-bearing transparency onto and from the photopolymerizable surface after exposure in a vacuum frame. (An image-bearing transparency may also be referred to herein as a mask, target, silver halide target, and phototool.) The release layer provides a substantially non-tacky surface to the typically tacky surface of the photopolymerizable

layer. The release layer can also protect the surface of the photopolymerizable layer from being damaged during removal of an optional temporary coversheet and can ensure that the photopolymerizable layer does not stick to the coversheet. When the thermally removable layer is functioning as a release layer, the layer is transparent or substantially transparent, i.e., insensitive or substantially insensitive, to actinic radiation.

('859 Patent at col. 10, lines 1-15.)

DuPont's proposed construction comes from the final sentence above, but Dupont fails to take into account the remainder of the specification's "release layer" discussion. The proposed construction also is inconsistent with the actual language of claim 21 itself, which refers to an additional layer selected from the group consisting of a "release layer, adhesion-modifying layer, barrier layer, and surface modifying layer, wherein the at least one more additional layer is transparent to actinic radiation." (Id. at col. 45, lines 17-21 (emphasis added).)

But MacDermid recommends an unduly narrow construction of this term, overlooking language in the specification regarding the presence of a release layer in digital imaging. The Court, in the Preliminary Injunction Opinion, addressed the term in the context of tentatively construing the term "thermally removable layer". (Prelim. Inj. Op. at 33-36.) Quoting the specification, the Court noted that "[a] release layer can also be used with digital imaging." (Id. at 35 (citing '859 Patent at col. 40, lines 1-17).) Specifically, the specification describes an

example of digital imaging where the plate structure includes a release layer. (Id.)

The Court therefore rejects each proposed construction. Returning to the specification passage quoted above, it appears that the patent essentially characterizes a "release layer" as a "substantially non-tacky surface". ('859 Patent at col. 10, lines 6-7.) The Court construes the term "release layer" as referring to "a substantially non-tacky surface."

**b. "surface modifying layer"**

The term "surface modifying layer" presents the same kind of problems presented for "filler" and "particulate material." But MacDermid actually contends that the term itself is indefinite because the specification omits any "discussion of what surface is modified; what characteristic of the surface is modified; and/or how the surface is modified." (MacDermid Opening Br. at 44.) According to MacDermid, "the ordinary meaning of the common terms 'surface' and 'modifying' do not correct the deficiencies in the specification." (Id. (citing dictionary definitions).) DuPont contends that (1) the term need not be construed because it would be readily understood by a person of ordinary skill in the art, and (2) MacDermid's indefiniteness position is contradicted by the specification itself. (Tr. at 58-61.)

DuPont thereby cites to specification language providing a relatively clear definition of the term at issue. The

Case 3:06-cv-03383-MLC-TJB Document 310 Filed 03/15/10 Page 39 of 41 PageID: 9298

specification refers to the thermally removable layer functioning as "a layer which alters the surface characteristics of the photosensitive element." ('859 Patent at col. 9, lines 62-63.) This Court accordingly construes "surface modifying layer" as meaning "a layer that alters the surface characteristics of photosensitive element." For good cause appearing:

**IT IS THEREFORE** on this 15th day of March, 2010,

**ORDERED** that the Court finds that, in United States Patent No.

6,171,758 B1:

**THE TERM "DIMENSIONALLY STABLE"** in claim 1 is construed to mean: "A flexible polymeric substrate whose dimensional stability has been controlled through a special annealing process, namely an annealing process that: (1) is in addition and subsequent to the heat treating steps associated with manufacturing the polymeric film, (2) is not the process of bonding the photosensitive elastomer layer to the polymeric substrate, and (3) comprises: (i) heating the substrate to a temperature above its glass transition temperature but below its melting temperature and at or greater than the temperature to which the substrate is later subjected during thermal development, (ii) at tensions of less than 200 psi, and (iii) for a time greater than the time required to bring the film to the annealing temperature, such that a specially annealed substrate has less thermally induced distortion than a non-specially annealed substrate"; and

**THE TERM "THERMAL DISTORTION"** in claim 1 is construed to mean: "the magnitude of change in the machine and transverse direction caused by thermal development of the flexographic printing plate"; and

**THE TERM "DEVELOPED"** in claim 1 is construed to mean: "removal of unexposed, uncured portions of the photosensitive elastomer layer"; and

**THE TERM "THERMOPLASTIC ELASTOMERIC BLOCK COPOLYMER"** in claim 4 is construed to mean: "a class of polymeric materials composed of two or more comonomeric units in extended segments having hard and soft blocks"; and

**IT IS FURTHER ORDERED** that the Court finds that, in United States Patent No. 6,773,859 B2:

**THE TERM "SOFTENING OR MELTING TEMPERATURE"** in claim 1 is construed to mean: "any temperature at which the viscosity of the binder will be reduced to such a point that the thermally removable layer, or portions thereof, may be removed"; and

**THE TERM "FILLER"** in claim 1 does not require construction; and

**THE TERM "PARTICULATE MATERIAL"** in claim 1 does not require construction; and

**THE TERM "RELEASE LAYER"** in claim 21 is construed to mean: "a substantially non-tacky surface"; and

**THE TERM "SURFACE MODIFYING LAYER"** in claim 21 is construed to mean: "a layer that alters the surface characteristics of the photosensitive element."

---

s/Mary L. Cooper  
**MARY L. COOPER**  
United States District Judge



US006171758B1

(12) **United States Patent**  
**Bhateja et al.**

(10) **Patent No.:** **US 6,171,758 B1**  
(45) **Date of Patent:** **Jan. 9, 2001**

(54) **DIMENSIONALLY STABLE FLEXOGRAPHIC PRINTING PLATES**

(75) Inventors: **Sudershan K. Bhateja**, Cottage Grove; **John A. Martens**, Dellwood; **Kurt F. Feil**, Lake Elmo, all of MN (US)

(73) Assignee: **DuPont Operations Worldwide, Inc.**, Wilmington, DE (US)

(\*) Notice: Under 35 U.S.C. 154(b), the term of this patent shall be extended for 0 days.

(21) Appl. No.: **08/335,892**

(22) Filed: **Nov. 8, 1994**

(51) **Int. Cl.<sup>7</sup>** ..... **G03C 1/73**

(52) **U.S. Cl.** ..... **430/271.1**; 430/306; 430/11

(58) **Field of Search** ..... 430/271, 306, 430/11

(56) **References Cited**

U.S. PATENT DOCUMENTS

2,779,684	1/1957	Alles .
3,264,103	8/1966	Cohen et al. .
3,632,726	1/1972	Knox et al. .
4,042,569	8/1977	Bell et al. .
4,076,532	2/1978	Gottermeier .
4,141,735	2/1979	Schrader et al. .
4,160,799	7/1979	Locey et al. .
4,275,107	6/1981	Bartkus et al. .
4,308,342	12/1981	Limoges et al. .
4,400,459	8/1983	Gruetzmacher et al. .
4,569,885	2/1986	Yamaguchi et al. .
4,661,377	4/1987	Morita et al. .

4,686,172 *	8/1987	Worns et al. ....	430/286
4,710,421	12/1987	Ono et al. .	
4,725,479	2/1988	Utsumi .	
4,756,953	7/1988	Utsumi .	
4,799,772	1/1989	Utsumi .	
4,847,033	7/1989	Carroll, Jr. .	
5,015,556	5/1991	Martens .	
5,085,976	2/1992	Gibson, Jr. et al. .	
5,175,072 *	12/1992	Martens ....	430/286
5,187,044	2/1993	Prioleau et al. .	
5,215,859	6/1993	Martens .	
5,279,697	1/1994	Peterson et al. .	

FOREIGN PATENT DOCUMENTS

14 47 030	1/1969	(DE) .
0 408 197	1/1991	(EP) .

OTHER PUBLICATIONS

19809 "Method for preparing dimensionally stable polymeric film" Research Disclosure, Oct., 1980, p. 411-412.

\* cited by examiner

*Primary Examiner*—Laura Weiner  
*(74) Attorney, Agent, or Firm*—Thomas H. Magee

(57) **ABSTRACT**

The present invention is a flexographic printing plate having a very low degree of thermal distortion during development. This flexographic printing plate comprises a dimensionally stable substrate and an image bearing relief layer, wherein the thermal distortion of the flexographic printing plate in both the machine and the transverse directions is less than 0.02% when the plate is developed at temperatures in the range from about 100° C. to about 180° C.

**21 Claims, No Drawings**

US 6,171,758 B1

1

## DIMENSIONALLY STABLE FLEXOGRAPHIC PRINTING PLATES

## FIELD OF THE INVENTION

The present invention relates to dimensionally stable flexographic printing plates.

## BACKGROUND OF THE INVENTION

Flexography is a term broadly applicable to a printing format that uses a flexible substrate bearing an elastomeric or rubbery relief printing surface. The first flexographic printing plates were produced from natural or synthetic rubber compositions which were cured chemically under heat and pressure in a mold utilizing conventional rubber curatives such as mercapto compounds (*Flexography: Principles and Practices*, 3rd Edition, Flexographic Technical Association, p. 158-162). More recently, photopolymer elastomeric compositions (elastomer containing compositions curable upon exposure to actinic radiation) have been used to produce relief printing plates. For example, U.S. Pat. No. 4,162,919 describes the use of a photosensitive composition containing a block copolymer as an elastomeric polymeric binder, a compatible ethylenically unsaturated monomer, and a photoinitiator. Similarly, British Pat. No. 1,454,191 describes the use of an elastomeric polyurethane based photosensitive layer. In both cases, the standard solvent wash procedure is used to develop the relief layer after exposure to actinic radiation. European Pat. No. 261,910 describes an aqueous-developable flexographic printing plate.

Both the solvent wash and aqueous wash developing systems are time consuming since drying for extended periods (1 to 24 hours) is necessary to remove entrained developer solution. In addition, these developing systems produce potentially toxic by-product wastes (both the solvent and any material carried off by the solvent, such as unreacted ethylenically unsaturated monomer) during the development process.

To avoid these problems, a thermal development process may be used. In a thermal development process, the photosensitive layer, which has been image-wise exposed to actinic radiation, is contacted with an absorbent layer at a temperature sufficient to cause the composition in the unexposed portions of the photosensitive layer to soften or melt and flow into the absorbent material. See U.S. Pat. Nos. 3,264,103, 5,015,556, and 5,279,697.

## SUMMARY OF THE INVENTION

The present invention is a flexographic printing plate having a very low degree of thermal distortion during development. Specifically, according to a preferred embodiment the invention is a flexographic printing plate comprising a dimensionally stable substrate and an image bearing relief layer, wherein the thermal distortion of the flexographic printing plate in both the machine and the transverse directions is less than 0.02% when the plate is developed at temperatures in the range from about 100° C. to about 180° C.

## DETAILED DESCRIPTION OF THE INVENTION

In the development of thermally developable flexographic printing plates, we have discovered that thermal distortion may become a problem, especially when precise lines, points, and images are desired by the printers who are using

2

the plates. In response to this newly discovered problem, we have developed printing plates that can withstand the developing temperatures without undergoing a significant amount of distortion.

“Developing temperature” is the temperature to which the imagewise exposed photosensitive layer is heated to remove the uncured portions of the layer. Although a variety of methods may be used for thermal development of flexographic printing plates, one method of development uses the apparatus disclosed in U.S. Pat. No. 5,279,697. In this method, the temperature of the developing roll which contacts the absorbent material approximates the developing temperature. The substrate, which is on the opposite side from the developing roll, does not reach the developing temperature in this embodiment. In fact, the substrate may be 15 to 30° C. cooler than the developing roll. However, if other methods of thermal development are utilized the entire plate may be heated to the developing temperature.

According to a preferred embodiment the invention is a flexographic printing plate comprising a dimensionally-stable, flexible, polymeric substrate and an elastomeric, image bearing, relief layer. The thermal distortion (includes both elongation and shrinkage) of the plate in both the machine and the transverse directions is less than 0.03%, preferably less than 0.025%, more preferably less than 0.020%, when the plate is developed at temperatures between 100 and 180° C. The distortion experienced during the development of the plate at 120 to 175° C. is preferably less than 0.015%. The machine direction is the direction that the substrate film is pulled during production. The transverse direction is perpendicular to the machine direction in the plane of the substrate. Such balanced, low distortion is critical to achieving flexographic printing plates which do not introduce distortion into the image which is to be reproduced.

According to a second preferred embodiment, the invention is a flexible plate comprising a dimensionally stable, flexible, polymeric substrate and a photosensitive elastomer layer. The polymeric substrate experiences less than 0.07% distortion, preferably less than 0.05% distortion, more preferably less than 0.03% distortion, even more preferably less than 0.025%, and most preferably less than 0.02%, in any planar direction when heated to temperatures from 110 to 180° C. The distortion is desirably less than 0.02% when the film is heated to temperatures from 140 to 150° C.

The substrate may be 0.07 to 2 mm thick and is preferably 0.1 to 1.5 mm thick. While a variety of polymeric materials may be used as the substrate, semicrystalline polymers are particularly desirable because these polymeric materials are particularly amenable to stabilization by thermal annealing. Examples of semicrystalline polymers include polyethylene naphthalate (PEN), polyethylene terephthalate (PET), polyether ketone, polytetrafluoroethylene, polyamides, syndiotactic polystyrene, and polyphenylene sulfide.

The desirability of such semicrystalline polymers arises from the discovery that dimensional stability of these polymer substrates may be controlled through a special annealing process. This annealing process comprises heating the polymer substrates to temperatures above their glass transition temperature and below their melting temperature. If this annealing occurs at low tensions, very little thermal distortion will occur when the substrate is later subjected to temperatures which are less than the annealing temperature. In fact, if the substrate is later heated to temperatures less than or equal to the annealing temperature minus about 25° C. (i.e.,  $T_{anneal} - 25$ ° C.), the thermal distortion has been

## US 6,171,758 B1

## 3

found to be less than 0.05%. If the substrate is heated to temperatures less than the annealing temperature minus about 30 or 40° C. (i.e.,  $T_{\text{anneal}}-30$  or 40° C.), the thermal distortion has been found to be less than 0.03%. By low tensions is meant tensions less than about 200 psi ( $1.4 \times 10^6$  N/m<sup>2</sup>), preferably less than about 150 psi ( $1.04 \times 10^6$  N/m<sup>2</sup>), and more preferably less than about 100 pounds per square inch ( $6.9 \times 10^5$  N/m<sup>2</sup>). High tension annealing causes distortions. Various annealing methods may be used including air-oven annealing, hot can annealing, annealing rolls of films, or combinations of methods.

The time required for annealing will depend upon the annealing method employed, the polymeric material of the film, film thickness, etc. With regard to the method of annealing, heat transfer by conduction, as occurs in hot can annealing, is more efficient than by convection, as occurs in air oven annealing. Thus, the annealing time for air oven annealing will be longer than that needed for hot can annealing. As an example, for annealing a 7 mil PET film in a forced air oven at 180° C., annealing times as low as 60 seconds were found to be sufficient to impart dimensional stability to the film. In general, however, for any given annealing method, the annealing time should be greater than the time required to bring the film to the annealing temperature (referred to hereinafter as " $t_h$ "), preferably  $t_h+5$  seconds, more preferably  $t_h+10$  seconds, and most preferably  $t_h+15$  seconds.

Thus, by annealing the substrates to preferably at least 25° C., more preferably at least 30° C., and most preferably at least 40° C., higher than the temperature the substrates experience during thermal development of the flexographic printing plate, the distortion of the printing plate during thermal development is significantly decreased. For plates being thermally developed using the apparatus of U.S. Pat. No. 5,279,697, the substrate should preferably be annealed at temperatures no less than about 10° C. below the developing temperature as approximated by the temperature of the developing roller (i.e.  $T_{\text{developing}}-10$ ° C.), more preferably no less than the developing temperature, and most preferably no less than the developing temperature plus 15° C.

Thermal development of preferred flexographic printing plates occurs by contacting a plate which has been image-wise exposed to radiation to an absorbent material on a developing roll. Typically, temperatures of the developing roll are in the range of 100 to 180° C. For A-B-A block copolymer type photosensitive materials as described below and in copending U.S. application Ser. No. 08/188,450, the developing roll temperature is preferably 120 to 150° C. Thus, for production of these plates, annealing of the substrate is preferably done at low tensions and at temperatures greater than 120° C., more preferably greater than 150° C., and most preferably greater than 175° C. For urethane type photosensitive materials as described below and in U.S. Pat. No. 5,015,556, the developing roll temperature is preferably about 150 to 175° C. Thus, for production of these plates, annealing of the substrate is preferably done at low tensions and at temperatures greater than 150° C., more preferably greater than 175° C., and most preferably greater than 200° C. However, even annealing below the developing temperature provides some improvement in shrinkage over substrates that are not annealed. Note that for certain semicrystalline polymeric materials annealing at too high a temperature may cause problems such as wrinkling. For example, polyethylene terephthalate (PET) has been found to wrinkle when annealed at 220° C.

The substrate optionally may be surface treated for better adhesion. Examples of surface treatments include coating

## 4

the surface with MSOL (an amorphous porous silica with silane coupling agent) as described in U.S. Pat. No. 5,204,219 or corona treating the surface followed by use of a primer such as an aziridene, as described in U.S. Pat. No. 5,187,044.

5 The photosensitive, elastomeric layer should be at least 0.3 mm thick but no more than 3.0 mm thick, preferably no more than 1.5 mm. The photosensitive elastomeric composition preferably is suitable for thermal development, i.e., the uncured elastomeric composition must soften or melt at a reasonable processing or developing temperature but not be subject to cold flow, i.e., dimensional change, during normal storage.

10 A non-limiting example of such an elastomeric composition comprises a thermoplastic elastomeric block copolymer mixed with a cross-linking agent and a photoinitiator. The elastomeric block copolymer is preferably an A-B-A type

block copolymer, where A is a nonelastomeric block, preferably a vinyl polymer and most preferably polystyrene and B is an elastomeric block, preferably polybutadiene or 15 polyisoprene. The nonelastomer to elastomer ratio is preferably in the range of from 10:90 to 35:65. The cross-linking agent in this embodiment may be an ethylenically unsaturated compound with at least one terminal ethylenic group that is compatible with the block copolymer, e.g., multi-functional acrylates or methacrylates, or polyacryloyl oligomers. The following compounds are illustrative of, but not 20 an exhaustive list of, suitable cross-linking agents: ethylene glycol diacrylate, hexanediol diacrylate, diethylene glycol diacrylate, glycerol diacrylate, trimethylol propane triacrylate, hexanediol dimethacrylate, glycerol triacrylate, 25 trimethylolpropane triacrylate, ethylene glycol dimethacrylate, 1,3-propanediol dimethacrylate, 1,2,4-butanetriol trimethacrylate, and 1,4-butanediol diacrylate. For a more exhaustive list of suitable compounds see U.S. 30 Pat. No. 4,400,459. A mixture of mono-functional and 35 multi-functional acrylates or methacrylates may be used. However, if using such a mixture, it is desirable to have an average of at least 1.3 acrylate groups per molecule of cross-linking agent. It is preferable to have an average of at 40 least 1.7 acrylate groups per molecule of cross-linking agent, and it is most preferable to have at least 2.1 acrylate groups per molecule of cross-linking agent. If a polyacryloyl oligomer is used, that oligomer should preferably have a 45 molecular weight greater than 1000.

45 Other suitable photosensitive elastomers that may be used include polyurethane elastomers. An example of a suitable polyurethane elastomer is the reaction product of (i) an organic diisocyanate, (ii) at least one chain extending agent having at least two free hydrogen groups capable of polymerizing with isocyanate groups and having at least one 50 ethylenically unsaturated addition polymerizable group per molecule, and (iii) an organic polyol with a minimum molecular weight of 500 and at least two free hydrogen containing groups capable of polymerizing with isocyanate groups. For a more complete discussion of some of these 55 materials see U.S. Pat. No. 5,015,556.

56 The photosensitive elastomeric layer should include a photoinitiator. The photoinitiator is a compound which generates free radicals upon exposure to actinic radiation. Any 60 of the known classes of photoinitiators, particularly free radical photoinitiators such as quinones, benzophenones, benzoin ethers, aryl ketones, peroxides, biimidazoles, diaryliodoniums, triarylsulfoniums and phosphoniums, and diazoniums, may be used. Alternatively, the photoinitiator 65 may be a mixture of compounds, one of which provides the free radicals when caused to do so by a sensitizer activated by radiation, may be used.

## US 6,171,758 B1

## 5

Additional additives to the photosensitive layer include colorants, processing aids, antioxidants, and antiozonants. Processing aids may be such things as low molecular weight polymers compatible with the elastomeric block copolymer, such as a low molecular weight  $\alpha$ -methylstyrene polymer or copolymer. Antiozonants include hydrocarbon waxes, norbornenes, and vegetable oils. Suitable antioxidants include alkylated phenols, alkylated bisphenols, polymerized trimethylidihydroquinone, and dilauryl thiopropionate.

The release layer must be flexible, transparent, coatable, and nontacky. A thin layer, preferably having a thickness of at least 0.5 microns, but less than 10 microns, more preferably less than 4 microns, is suitable.

The release layer preferably is removable by contact with an absorbent material in the range of acceptable developing temperatures for the flexographic plate used. Suitable release layers may include polyamides and hydroxy cellulosic polymers.

Additional intermediate photosensitive layers may be used to adjust adhesion, hardness, and thickness of the flexographic printing plate.

## EXAMPLES

## Example 1

Five mil (0.12 mm) polyethylene naphthalate (PEN) films (Kaladex 1,030 from ICI) were cut into 15" x 20" (38.1 cm x 50.8 cm) pieces. One film piece was not heated treated. This sample was the control. The other film pieces were annealed in a forced air oven for 5 minutes at various temperatures ranging from 140 to 200° C. Specimens (1" x 13" or 2.54 cm x 33.02 cm) were cut from the different films. The specimens were cut in both the machine and transverse directions. Two ink marks about 10.6" (26.9 cm) apart were made on each specimen. The distance between ink marks was measured with a Conformer Travelling Microscope. The specimens were then heated at 150° C. for 15 minutes. The distance between the ink marks was then remeasured and the distortion calculated. For each annealing temperature, two different specimens were measured for each direction. As set forth in Table I, all of the annealed specimens showed much less shrinkage in both the machine and transverse directions than did the control samples. The amount of distortion was well balanced between the machine and transverse directions. Samples that had been annealed close to or above the test temperature had the best thermal dimensional stability in terms of magnitude distortion and balance of distortion in the two directions.

TABLE 1

SAMPLE	(° C.)	ANNEALING TEMPERATURE		DISTORTION (%)
		machine dir.	transverse dir.	
Control	—	0.354	—	
Control	—	0.389	—	
Control	—	—	0.324	
Control	—	—	0.326	
Control	—	—	0.306	
A-1	140	0.086	—	
A-1	140	0.098	—	
A-1	140	0.061	—	
A-1	140	—	0.080	
A-1	140	—	0.063	
A-1	140	—	0.063	
A-2	160	0.009	—	

## 6

TABLE 1-continued

SAMPLE	(° C.)	ANNEALING TEMPERATURE		DISTORTION (%)
		machine dir.	transverse dir.	
A-2	160	0.018	—	
A-2	160	—	0.029	
A-2	160	—	0.046	
A-2	160	—	0.013	
A-3	180	-0.001	—	
A-3	180	0.013	—	
A-3	180	0.009	—	
A-3	180	—	0.023	
A-3	180	—	0.020	
A-3	180	—	0.024	
A-4	200	-0.001	—	
A-4	200	0.001	—	
A-4	200	0.011	—	
A-4	200	—	0.012	
A-4	200	—	0.001	
A-4	200	—	0.014	

## Example 2

Four PEN film samples were prepared. Two of the films had not been heat treated and served as the control. Two films had been annealed as in Example 1 for 5 minutes at 170° C. All the films, after any annealing was done, were inscribed with four straight lines 15 in. long (38.1 cm). One line was drawn along the transverse direction of the PEN film and this line was designated as the 0° line. The three additional lines were drawn at angles of 45°, 90°, and 135° from the 0° line. The film samples were cycled nine times through a flexographic plate thermal developer (as disclosed in U.S. Pat. No. 5,279,697) in which the developer roll was set at 176° C. and the transport drum (which contacts the substrate) was set at 65° C. The change of length of each line was measured and the percentage distortion was calculated. Table II shows that the annealed films displayed significantly less distortion than did the control films in all directions.

TABLE II

SAMPLE	POSITION	DISTORTION (%)
Control 1	0°	-0.106
Control 2	0°	-0.152
Annealed 1	0°	-0.005
Annealed 2	0°	-0.006
Control 1	45°	-0.122
Control 2	45°	-0.124
Annealed 1	45°	0.004
Annealed 2	45°	-0.021
Control 1	90°	-0.030
Control 2	90°	-0.069
Annealed 1	90°	0.005
Annealed 2	90°	-0.007
Control 1	135°	-0.070
Control 2	135°	-0.093
Annealed 1	135°	-0.007
Annealed 2	135°	-0.009

## Example 3

Flexographic printing plates were produced using various PEN film substrates. Four of the plates produced had standard 5 mil (0.127 mm) Kaladex™ brand PEN substrates. Three plates were produced using the same type of PEN film, but after the film had been annealed at 170° C. for 5 minutes. The substrates were corona discharge treated and

## US 6,171,758 B1

7

coated with an aziridine primer as disclosed in U.S. Pat. No. 5,187,044. Then a 35 mil urethane photopolymer, as disclosed in U.S. Pat. No. 5,215,859 Example 1A, was laminated onto the primed films between two rolls heated to 110° C. The laminates were exposed to e-beam irradiation through the substrate to set the film. The laminates were next image wise exposed to UV radiation through a GATF Register test grid negative for 3 minutes. The image wise exposed plates were passed through 6 cycles on the thermal developer. The developer roll was maintained at 177° C. while the transport roll, which is in direct contact with the substrate, was maintained at 65° C. The magnitude of distortion in the machine and transverse directions was determined by measuring the developed image on the flexographic printing plates versus the image on the negative. Negative distortion values refer to shrinkage and positive values refer to expansion. Table III shows the average distortion results for the control plates and the plates with annealed substrates. These results demonstrate that the plates produced from the annealed PEN films have lower distortion than do plates produced with unannealed substrates.

TABLE III

Sample	Distortion (%)*	
	machine direction	transverse direction
Control**	-0.0333	-0.0131
Annealed***	-0.0086	0.0066

\*Average of 3 measurements in each direction.

\*\*Average for 4 plates.

\*\*\*Average for 3 plates.

## Example 4

Flexographic printing plates were also produced using both thermally annealed and non-annealed 7-mil (0.178 mm) polyethylene terephthalate (PET) film substrates. The thermally annealed film was produced on-line in an air oven held at about 160° C. with a web tension of about 100 psi ( $6.9 \times 10^5$  N/m<sup>2</sup>). The film substrates were corona treated and primed as in Example 3. Approximately 18"×20" (45.7 cm×50.8 cm) treated film specimens were laminated with a 60 mil thick Kraton™ based photosensitive elastomeric composition. The plate specimens were then imaged through a negative having an x-y grid and 45° angle lines. The imaged plates were developed by cycling 6 times through the processor of U.S. Pat. No. 5,279,697. The developer roll was at 176° C. and the transport drum was at 65° C. Some plates were fed through the thermal developer unit in the machine direction, while others were fed crosswise (or in the transverse direction) through the processor. The magnitude of plate distortion was calculated with respect to the negative by measuring changes in a grid, 12 inch (30.5 cm) in the machine direction (MD) and 10 inch (25.4 cm) in the transverse direction (TD). For each plate three different measurements were made in each direction. Negative distortion values refer to shrinkage and positive values refer to expansion. The data shown in Table IV demonstrates that plates produced with annealed PET substrates exhibit lower distortion than plates produced with non-annealed PET substrates.

8

TABLE IV

SAMPLE	PROCESSING DIRECTION	DISTORTION (%)*	
		MD	TD
Annealed-1	Machine	0.007	0.007
Annealed-2	Machine	-0.014	-0.007
Annealed-3	Machine	0.008	0.013
Annealed-4	Machine	-0.014	-0.008
Annealed-5	Cross	-0.007	-0.006
Annealed-6	Cross	-0.025	0.023
Annealed-7	Cross	-0.011	-0.014
Control-1**	Machine	-0.073	-0.051
Control-2**	Cross	-0.053	-0.037

\*Average of 3 measurements in each direction for each plate

\*\*Average of 3 plates

What is claimed is:

1. A photosensitive plate suitable for use as a flexographic printing plate comprising a dimensionally stable, flexible, polymeric substrate and a photosensitive elastomer layer, wherein the plate has a thermal distortion in both the machine and the transverse directions which is less than 0.03% when the plate is exposed to actinic radiation and, after exposure, is developed at temperatures between 100 and 180° C.
2. The plate of claim 1 wherein the thermal distortion is less than 0.015% when the plate is developed at temperatures from 120 to 175° C.
3. The plate of claim 1 wherein the substrate has a thickness from 0.07 to 2 mm.
4. The plate of claim 1 wherein the photosensitive elastomer layer comprises a thermoplastic elastomeric block copolymer mixed with a cross-linking agent and a photoinitiator.
5. The plate of claim 4 wherein the elastomeric block copolymer is an A-B-A type block copolymer, where A is a vinyl polymer and B is polybutadiene or polyisoprene and the ratio A:B is in the range of from 10:90 to 35:65, and the cross-linking agent is an ethylenically unsaturated compound with at least one terminal ethylenic group that is compatible with the block copolymer.
6. The plate of claim 1 wherein the photosensitive elastomer layer comprises a polyurethane elastomer which is the reaction product of (i) an organic diisocyanate, (ii) at least one chain extending agent having at least two free hydrogen groups capable of polymerizing with isocyanate groups and having at least one ethylenically unsaturated addition polymerizable group per molecule, and (iii) an organic polyol with a minimum molecular weight of 500 and at least two free hydrogen containing groups capable of polymerizing with isocyanate groups.
7. The plate of claim 1 wherein the polymeric substrate is a semicrystalline polymer.
8. The plate of claim 7 wherein the semicrystalline polymer is selected from the group consisting of: polyethylene naphthalate, polyethylene terephthalate, polyether ketone, polytetrafluoroethylene, polyamide, syndiotactic polystyrene, and polyphenylene sulfide.
9. The plate of claim 7 wherein the semicrystalline polymer substrate has been annealed at tensions less than  $1.4 \times 10^6$  N/m<sup>2</sup> and a temperature, which is between the glass transition temperature and the melting temperature and is greater than the developing temperature minus 10° C.
10. The plate of claim 9 wherein the annealing temperature is greater than the developing temperature plus 15° C.
11. The plate of claim 9 wherein the annealing temperature is greater than the developing temperature.

US 6,171,758 B1

**9**

12. The plate of claim **9** wherein the annealing temperature is greater than 120° C.

13. The plate of claim **9** wherein the annealing temperature is greater than 150° C.

14. The plate of claim **9** wherein the annealing temperature is greater than 175° C.

15. The plate of claim **9** wherein the annealing is performed at tensions of less than  $6.9 \times 10^5$  N/m<sup>2</sup>.

16. The plate of claim **9** in which the substrate has been annealed for a time greater than the time it takes for the substrate to reach the annealing temperature.

17. The plate of claim **9** wherein the polymer substrate is annealed for a time greater than the time required to reach the annealing temperature plus 5 seconds.

18. The plate of claim **12** in which the polymer substrate is annealed by air-oven annealing, hot can annealing, annealing rolls of film, or combinations of these methods.

**10**

19. A photosensitive plate suitable for use as a flexographic printing plate comprising a dimensionally stable, flexible, polymeric substrate and a photosensitive elastomer layer, wherein said polymeric substrate experiences less than 0.07% distortion in any planar direction when heated to temperatures from 110 to 180° C.

20. The plate of claim **19** wherein the substrate experiences less than 0.05% distortion in any planar direction when heated to temperatures from 110 to 180° C.

21. The plate of claim **19** wherein the substrate experiences less than 0.02% distortion in any planar direction when heated to temperatures from 110 to 180° C.

\* \* \* \* \*



US006773859B2

**(12) United States Patent**  
Fan et al.

**(10) Patent No.:** US 6,773,859 B2  
**(45) Date of Patent:** Aug. 10, 2004

**(54) PROCESS FOR MAKING A FLEXOGRAPHIC PRINTING PLATE AND A PHOTOSENSITIVE ELEMENT FOR USE IN THE PROCESS**

**(75) Inventors:** **Roxy Ni Fan**, Warren, NJ (US); **Mark A. Hackler**, Ocean, NJ (US); **Anandkumar R. Kannurpatti**, E. Windsor, NJ (US); **Adrian Lungu**, Old Bridge, NJ (US); **Bradley K. Taylor**, West Chester, PA (US)

**(73) Assignee:** **E. I. du Pont de Nemours and Company**, Wilmington, DE (US)

**(\*) Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 21 days.

**(21) Appl. No.:** 10/085,262

**(22) Filed:** Feb. 27, 2002

**(65) Prior Publication Data**

US 2003/0180655 A1 Sep. 25, 2003

**(51) Int. Cl.<sup>7</sup>** ..... G03F 7/34; G03F 7/095; G03F 7/11

**(52) U.S. Cl.** ..... 430/200; 430/254; 430/273.1; 430/306; 430/309; 430/327; 430/330

**(58) Field of Search** ..... 430/200, 254, 430/273.1, 306, 309, 327, 330

**(56) References Cited**

**U.S. PATENT DOCUMENTS**

3,060,024 A 10/1962 Burg et al.

3,060,025 A	10/1962	Burg et al.
3,264,103 A	8/1966	Cohen et al.
4,429,027 A	1/1984	Chambers, Jr. et al.
5,175,072 A	12/1992	Martens
5,262,275 A	11/1993	Fan
5,607,814 A	3/1997	Fan et al.
5,719,009 A	2/1998	Fan
5,840,463 A	11/1998	Blanchet-Fincher
5,888,697 A	3/1999	Fan
2002/0009672 A1	1/2002	Daems et al.

**FOREIGN PATENT DOCUMENTS**

EP	0665469 A2	8/1995
EP	0665471 A2	8/1995
EP	0741330 A1	11/1996

*Primary Examiner*—Richard L. Schilling

*(74) Attorney, Agent, or Firm*—Thomas H. Magee

**(57)**

**ABSTRACT**

The invention relates to a process for preparing a flexographic printing plate from a photosensitive element having a photopolymerizable layer and a thermally removable layer on the photopolymerizable layer. The process includes imagewise exposing the photosensitive element and thermally treating the exposed element to form a relief suitable for use in flexographic printing. The thermally removable layer can be transparent or opaque to actinic radiation. The invention also relates to a photosensitive element for use in this process. The photosensitive element includes a photopolymerizable layer and at least one thermally removable layer having a filler and a binder, wherein the binder is less than 49% by weight, based on the total weight of the binder and filler.

**54 Claims, No Drawings**

US 6,773,859 B2

1

**PROCESS FOR MAKING A FLEXOGRAPHIC PRINTING PLATE AND A PHOTOSENSITIVE ELEMENT FOR USE IN THE PROCESS**

**BACKGROUND OF THE INVENTION**

**1. Field of the Invention**

This invention relates to a process for making a flexographic printing plate. In particular, the process forms the plate using a photosensitive element having at least one thermally-removable layer on at least one photopolymerizable layer and heating the element to form a relief surface suitable for flexographic printing. The invention also relates to a photosensitive element having a thermally-removable layer, which after undergoing thermally processing, is suitable for use as a flexographic printing plate.

**2. Description of Related Art**

Flexographic printing plates are widely used for printing of packaging materials ranging from corrugated carton boxes to card boxes and to continuous web of plastic films. Flexographic printing plates can be prepared from photopolymerizable compositions, such as those described in U.S. Pat. Nos. 4,323,637 and 4,427,759. The photopolymerizable compositions generally comprise an elastomeric binder, at least one monomer and a photoinitiator. Photosensitive elements generally have a layer of the photopolymerizable composition interposed between a support and a coversheet or a multilayer cover element. Flexographic printing plates are characterized by their ability to crosslink or cure upon exposure to actinic radiation. Typically the plate is uniformly exposed through the backside of the plate to a specified amount of actinic radiation. Next, an imagewise exposure of the front-side of the plate is made through an image-bearing artwork or a template, such as a photographic negative or transparency (e.g. silver halide film) inside a vacuum frame to ensure intimate contact of the artwork to the plate surface. The plate is exposed to actinic radiation, such as an ultraviolet (UV) or black light. The actinic radiation enters the photosensitive material through the clear areas of the transparency and is blocked from entering the black or opaque areas. The exposed material crosslinks and becomes insoluble to solvents used during image development. The unexposed, uncrosslinked photopolymer areas under the opaque regions of the transparency remain soluble and are washed away with a suitable solvent leaving a relief image suitable for printing. Then the plate is dried. The printing plate can be further treated to remove surface tackiness. After all desired processing steps, the plate is mounted on a cylinder and used for printing.

However, developing systems that treat the element with a solution are time consuming since drying for extended period (0.5 to 24 hours) is necessary to remove entrained developer solution. In addition, these developing systems produce potentially toxic by-product wastes (both the solvent and any material carried off by the solvent) during the development process.

To avoid the problems with solution development, a "dry" thermal development process may be used. In a thermal development process, the photosensitive layer, which has been imagewise exposed to actinic radiation, is contacted with an absorbent material at a temperature sufficient to cause the composition in the unexposed portions of the photosensitive layer to soften or melt and flow into an absorbent material. See U.S. Pat. Nos. 3,264,103 (Cohen et al.); U.S. Pat. No. 5,015,556 (Martens); U.S. Pat. No. 5,175,072 (Martens); U.S. Pat. No. 5,215,859 (Martens);

2

and U.S. Pat. No. 5,279,697 (Peterson et al.). In all these cited patents imagewise exposure is conducted with a silver halide film target in a vacuum frame. The exposed portions of the photosensitive layer remain hard, that is, do not soften or melt, at the softening temperature for the unexposed portions. The absorbent material collects the softened un-irradiated material and then is separated and/or removed from the photosensitive layer. The cycle of heating and contacting the photosensitive layer may need to be repeated several times in order to sufficiently remove the flowable composition from the un-irradiated areas and form a relief structure suitable for printing. Thus remains a raised relief structure of irradiated, hardened composition that represents the desired printing image.

The photosensitive element for flexographic use typically includes one or more additional layers on the photopolymerizable layer on the side opposite the support, that is, sandwiched between the photopolymerizable layer and the coversheet. The one or more additional layers can be, for instance, a release layer for ease in removing the image-bearing transparency (mask film) after exposure under vacuum, an elastomeric capping layer, or a radiation opaque layer. The radiation opaque layer is used to form a mask in situ on or above the photopolymerizable layer. Since the radiation opaque layer typically is also sensitive to infrared-radiation, the radiation opaque layer is exposed imagewise to infrared laser radiation to form an image on the photopolymerizable layer, i.e., the in situ mask. The infrared laser radiation can selectively remove or ablate the infrared sensitive layer (i.e., radiation opaque layer) from the photosensitive element, as disclosed by Fan in U.S. Pat. Nos. 5,262,275 and 5,719,009; Fan in EP 0 741 330 A; and Van Zoeren in U.S. Pat. No. 5,506,086; or can selectively transfer the infrared sensitive material onto the photopolymerizable layer of the element as disclosed by Fan et al. in U.S. Pat. No. 5,607,814; and Blanchett in U.S. Pat. Nos. 5,766,819; 5,840,463; and EP 0 891 877 A. One or more barrier layers may also be present between the photopolymerizable layer and the radiation opaque layer to maintain the integrity of the radiation opaque layer on the photopolymerizable layer. Thereafter, the element is overall exposed with actinic radiation through the mask and then wet processed, that is, in a solvent or aqueous solution, to form the relief as described above.

U.S. Pat. No. 5,888,697 discloses a photosensitive element having an overall layer of powder material on a photopolymerizable layer. The layer of particulate material can be opaque or transparent depending on desired use. A transparent powder layer can function as a release layer for the photosensitive element. The opaque powder layer can function as the radiation opaque layer for the photosensitive element as explained above. The powder material can be organic, inorganic, mixtures of organic and inorganic compounds, or multicomponent. The particle size of the powder material is less than 50 microns. After imagewise exposure, the relief is formed in the photosensitive element by washing with a suitable developer selected from organic solutions, water, aqueous, or semi-aqueous solutions. Thus, only conventional wet processing to form the relief image was disclosed.

EP 0 665 471 A2 discloses thermally developable flexographic printing plates having a release layer on a photosensitive elastomeric layer. The release layer is composed of a cellulose-based polymer, such as hydroxylalkyl cellulose, which has a softening point and melt viscosity compatible with the softening temperature of the photosensitive elastomeric layer forming the relief layer. The preferred develop-

## US 6,773,859 B2

## 3

ing temperatures range from 95° C. to about 150° C. The cellulose-based polymer of the release layer has a softening temperature less than about 130° C. However, not all hydroxyalkyl cellulose compounds were appropriate as the release layer for thermally developed plates. Hydroxyalkyl cellulose having too high a molecular weight was too viscous at the desired thermal developing temperatures. EP 0 665 471 A2 also discloses that a layer of polyvinyl alcohol on a photosensitive elastomeric layer does not melt sufficiently for thermal development.

U.S. Pat. No. 3,060,024 discloses a photopolymerization process for reproducing images using a thermoplastic element composed of a thermoplastic organic polymer, an ethylenically unsaturated compound with a terminal ethylenic group and a photoinitiator. In the process, the thermoplastic element is exposed imagewise to actinic light through a target in a vacuum frame, heated to the tack temperature, and dusted with finely-divided solid particles of material. The particles remain in the unexposed image areas that become tacky during the heating step, and are removed from the exposed image areas that are non-tacky after cooling to room temperature. Then the dusted surface of the thermoplastic element is contacted to a separate image-receptive element at a transfer temperature of at least 40° C. Transfer temperatures is the temperature at which the image areas stick or adhere within 10 seconds under slight pressure to a filter paper, and is between 40 and 170° C. The thermoplastic element is separated from the separate element so that the particles and an adherent portion of the unexposed image areas transfer to the surface of the image-receptive element. The process of heating, dusting, contacting and heating can be repeated multiple times to provide copies of the image. Example XII discloses using carbon having a particle size of 73 micrometers on the thermoplastic element. The unexposed areas of the photopolymerized layer with the toned particle material transferred to a paper support to form a black relief image, 3 mils in thickness. The transferred relief was post-exposed for use in relief printing.

U.S. Pat. No. 3,060,025 discloses a process similar to that of U.S. Pat. No. 3,060,024, except that the particles can be coated on a separate surface and transferred upon contact to the unexposed areas (but not the exposed areas) of the thermoplastic element upon application of heat. Binders may be used to adhere the coated particle layer to a support surface. For both U.S. Pat. No. 3,060,024 and 3,060,025, the thermoplastic element is imagewise exposed prior to contacting with particles or a particle layer. Thus, the particle layer is not present during the imagewise exposure to actinic light.

U.S. Pat. No. 3,264,103 discloses photopolymerizable relief printing plates developed by a dry thermal transfer process. The plate is made from a photopolymerizable printing element composed of a polymeric binder, an ethylenically unsaturated compound, and a polymerization photoinitiator. The process includes exposing the photopolymerizable element through an image-bearing transparency, heating the element to a temperature between the flow temperatures of the exposed and the unexposed areas, and absorbing molten unexposed material into a porous matrix element by pressing into contact the element and the porous matrix element. The heating operating temperature is between 40 and 260° C. The photopolymerizable layer of the element may include dyes and pigments, as well as fillers or reinforcing agents of sufficiently small particle size to penetrate the porous material.

Even though thermal processing of flexographic plates was disclosed by Martens in U.S. Pat. Nos. 5,015,556;

## 4

5,175,072; and 5,215,859, there was no comparative analysis of the differences in plate performance between the thermally processed plates and solvent processed plates. Dramatic reduction in plate performance have been found as 5 a result of thermal processing of plates. Problems have also been found with thermal development of photosensitive elements having the one or more additional layers on the photopolymerizable layer. The additional layers may not be adequately removed by heating at the temperature sufficient 10 to soften (or melt) to remove the unpolymerized portions of the photopolymerizable layer. All or parts of the additional layers may remain on the photosensitive element even after multiple cycles of heating and contacting with an absorbant material that are conducted in thermal development. The 15 portions of the additional layer/s that remain after thermal development can alter the relief depth, reverse depth, and surface of the plate and therefore detrimentally impact printing performance of the plate.

Further, it is desireable to minimize the time and temperature 20 at which the photosensitive element is held during thermal development to maintain the productivity of the system and to avoid distortion of the support or distortion of the fine image areas on the plate. Yet the desire to minimize time and temperature for thermal development must be balanced with the need to thoroughly remove (i.e., clean out) 25 the unpolymerized areas from the photopolymerized layer including the fine reverses as well as remove the one or more additional layers. The unpolymerized areas must be removed to form sufficient printing relief to use the element 30 as a plate. The additional layers must also be removed particularly from the surface and in between fine reverses in order for the plate to have quality printing of highlight dots, fine lines, mid-tones and fine reverses. Thus, a thermally processed photosensitive element should provide good processing latitude and excellent printing quality regardless of 35 screen ruling.

## SUMMARY OF THE INVENTION

It is an object to provide a process for making a flexographic printing plate in which one or more additional layers 40 disposed above a photopolymerizable layer of a photosensitive element are thoroughly removed with unexposed portions of the photopolymerizable layer upon thermal development.

It is another object of this invention to provide a photosensitive element having one or more additional layers 45 disposed above a photopolymerizable layer and a process for thermally developing the photosensitive element that are not limited by the melting or softening temperature associated with material or materials in the one or more additional layers on the photopolymerizable layer.

It is a further object of this invention to provide a process 50 for making a flexographic printing plate that reduces the time for thermal development at a developing temperature suitable for removal of unpolymerized portions of a photopolymerizable layer as well as one or more additional layers on the photopolymerizable layer.

It is a still further object of this invention to provide a 55 photosensitive element suitable for thermal development which has good processing latitude and provides quality print performance regardless of screen ruling.

In accordance with this invention there is provided a process for making a flexographic printing plate comprising 60 providing a photosensitive element which comprises at least one photopolymerizable layer on a support comprising an elastomeric binder, at least one monomer, and a 65

US 6,773,859 B2

5

photoinitiator, and at least one thermally removable layer disposed above the photopolymerizable layer. The thermally removable layer is selected from the group consisting of: (a) an actinic radiation opaque layer comprising (i) at least one infrared absorbing material, (ii) a radiation opaque material, wherein (i) and (ii) can be the same or different, and at least one binder having a softening or melting temperature less than 190° C.; (b) a layer of a composition comprising at least one binder and filler, wherein the binder is less than 49% by weight based on the total weight of the binder and filler, and (c) a layer of particulate material having particle size of less than 23 micrometers. The process includes imagewise exposing the photopolymerizable layer to actinic radiation forming polymerized portions and unpolymerized portions and thermally treating the imagewise exposed element by heating to a temperature sufficient to remove the thermally removable layer and to remove the unpolymerized portions of the photopolymerizable layer and form a relief.

In accordance with another aspect of this invention there is provided a photosensitive element for use as a flexographic printing plate comprising (a) at least one photopolymerizable layer on a support comprising an elastomeric binder, at least one monomer and a photoinitiator, wherein the photopolymerizable layer in an unexposed state is capable of melting, softening, or flowing at a treating temperature of at least 40° C., and (b) at least one thermally removable layer disposed above the photopolymerizable layer, wherein the thermally removable layer comprises at least one binder and a filler, wherein the binder is less than 49% by weight based on the total weight of the binder and filler.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

The process of the present invention prepares a flexographic printing plate from a photosensitive element comprising a photopolymerizable layer and at least one thermally removable layer thereon and includes the steps of imagewise exposing, and thermally treating to form a relief surface. The photosensitive element is able to withstand the conditions associated with thermal processing. Uncured portions of the photopolymerizable layer as well as the thermally removable layer/s thereon can be effectively removed to provide a relief plate suitable for high quality flexographic printing. In addition, the photosensitive element used in the present process is able to reproduce the fine picture elements from the desired image without distortion. Such a photosensitive element will allow one to use processing conditions that will not be detrimental to the fine features of the plate and/or a support for the element. Additionally, the photopolymerizable elastomeric layer of the photosensitive elements useful in this invention can be effectively processed in less number of cycles of heating and contacting and/or at lower temperatures. Also, the photosensitive element provides wide exposure and processing latitude.

The first step of the present process is to provide a photosensitive element. The photosensitive element comprises, in order, a support, at least one photopolymerizable layer, and at least one thermally removable layer on the photopolymerizable layer. As used herein, the term "photopolymerizable" is intended to encompass systems that are photopolymerizable, photocrosslinkable, or both. The photopolymerizable layer is formed of a composition comprising a thermoplastic binder, at least one monomer and a photoinitiator. The thermoplastic binder is preferably elastomeric. The photoinitiator has sensitivity to actinic

6

radiation. Throughout this specification actinic light will include ultraviolet radiation and/or visible light. The photopolymerizable composition is capable of partially liquefying upon thermal development. That is, during thermal development the uncured composition must soften or melt or flow at a reasonable processing or developing temperature but not be subject to cold flow, i.e., dimensional change, during normal storage.

The thermoplastic binder can be a single polymer or mixture of polymers. Binders include natural or synthetic polymers of conjugated diolefin hydrocarbons, including polyisoprene, 1,2-polybutadiene, 1,4-polybutadiene, and butadiene/acrylonitrile. Preferably, the thermoplastic binder is an elastomeric block copolymer of an A-B-A type block copolymer, where A represents a non-elastomeric block, preferably a vinyl polymer and most preferably polystyrene, and B represents an elastomeric block, preferably polybutadiene or polyisoprene. Suitable thermoplastic elastomeric binders of this type include poly(styrene/isoprene/styrene) block copolymers and poly(styrene/butadiene/styrene) block copolymers which are preferred. The non-elastomer to elastomer ratio is preferably in the range of from 10:90 to 35:65. Most preferably the thermoplastic elastomeric binder is a mixture of at least two poly(styrene/isoprene/styrene) block copolymers as described by Dudek et al. in U.S. Pat. No. 5,972,565. It is preferred that the binder be present in an amount of at least 60% by weight of the photosensitive layer.

The term binder, as used herein, encompasses core shell microgels and blends of microgels and preformed macromolecular polymers, such as those disclosed in Fryd et al., U.S. Pat. No. 4,956,252 and Quinn et al., U.S. Pat. No. 5,707,773.

Other suitable photosensitive elastomers that may be used include polyurethane elastomers. An example of a suitable polyurethane elastomer is the reaction product of (i) an organic diisocyanate, (ii) at least one chain extending agent having at least two free hydrogen groups capable of polymerizing with isocyanate groups and having at least one ethylenically unsaturated addition polymerizable group per molecule, and (iii) an organic polyol with a minimum molecular weight of 500 and at least two free hydrogen containing groups capable of polymerizing with isocyanate groups. For a more complete description of some of these materials see U.S. Pat. No. 5,015,556.

The photopolymerizable composition contains at least one compound capable of addition polymerization that is compatible with the binder to the extent that a clear, non-cloudy photosensitive layer is produced. The at least one compound capable of addition polymerization may also be referred to as a monomer and can be a single monomer or mixture of monomers. Monomers that can be used in the photopolymerizable composition are well known in the art and include, but are not limited to, addition-polymerization ethylenically unsaturated compounds with at least one terminal ethylenic group. Generally the monomers have relatively low molecular weights (less than about 30,000). Preferably, the monomers have a relatively low molecular weight less than about 5000. Examples of suitable monomers include, but are not limited to, t-butyl acrylate, lauryl acrylate, the acrylate and methacrylate mono- and polyesters of alcohols and polyols such as alkanols, such as hexanediol diacrylate and hexanediol dimethacrylate; alkylene glycols, such as ethylene glycol diacrylate, ethylene glycol dimethacrylate, and diethylene glycol diacrylate; trimethylol propane, such as trimethylol propane triacrylate; ethoxylated trimethylol propane; pentaerythritol; dipentaerythritol; polyacryloyl oligomers, and the like. If a poly-

## US 6,773,859 B2

7

acrylol oligomer is used, the oligomer should preferably have a molecular weight greater than 1000. A mixture of monofunctional and multifunctional acrylates or methacrylates may be used. Other examples of suitable monomers include acrylate and methacrylate derivatives of isocyanates, esters, epoxides and the like. Monomers can be appropriately selected by one skilled in the art to provide elastomeric property to the photopolymerizable composition. Examples of elastomeric monomers include, but are not limited to, acrylated liquid polyisoprenes, acrylated liquid butadienes, liquid polyisoprenes with high vinyl content, and liquid polybutadienes with high vinyl content, (that is, content of 1-2 vinyl groups is greater than 20% by weight). Further examples of monomers can be found in Chen U.S. Pat. No. 4,323,636; Fryd et al., U.S. Pat. No. 4,753,865; Fryd et al., U.S. Pat. No. 4,726,877 and Feinberg et al., U.S. Pat. No. 4,894,315. The compound capable of addition polymerization (monomer) is present in at least an amount of 5%, preferably 10 to 20%, by weight of the elastomeric composition.

The photoinitiator can be any single compound or combination of compounds which is sensitive to actinic radiation, generating free radicals which initiate the polymerization of the monomer or monomers without excessive termination. Any of the known classes of photoinitiators, particularly free radical photoinitiators such as quinones, benzophenones, benzoin ethers, aryl ketones, peroxides, biimidazoles, benzyl dimethyl ketal, hydroxyl alkyl phenyl acetophone, dialkoxy actophenone, trimethylbenzoyl phosphine oxide derivatives, aminoketones, benzoyl cyclohexanol, methyl thio phenyl morpholino ketones, morpholino phenyl amino ketones, alpha halogenoacetophenones, oxysulfonyl ketones, sulfonyl ketones, oxysulfonyl ketones, sulfonyl ketones, benzoyl oxime esters, thioxanthrones, camphorquinones, ketocoumarins, Michler's ketone may be used. Alternatively, the photoinitiator may be a mixture of compounds, one of which provides the free radicals when caused to do so by a sensitizer activated by radiation. Preferably, the initiator is sensitive to visible or ultraviolet radiation. Photoinitiators are generally present in amounts from 0.001% to 10.0% based on the weight of the photopolymerizable composition.

Optionally, the photopolymerizable layer can contain spectral sensitizing agents. In general, spectral sensitizing agents are those materials that absorb radiation at a wavelength different than that of the reaction-initiating component, i.e., photoinitiator, and are capable of transferring the absorbed energy to the photoinitiator. Thus, the wavelength of the activating radiation can be adjusted.

The photopolymerizable layer can contain other additives depending on the final properties desired. Additional additives to the photopolymerizable layer include sensitizers, plasticizers, rheology modifiers, thermal polymerization inhibitors, colorants, processing aids, antioxidants, antiozonants, and fillers. Processing aids may be such things as low molecular weight polymers compatible with the elastomeric block copolymer, such as low molecular weight alpha-methylstyrene polymer or copolymer. Antiozonants include hydrocarbon waxes, norbornenes, and vegetable oils. Suitable antioxidants include alkylated phenols, alkylated bisphenols, polymerized trimethyldihydroquinone, and dilauryl thiopropionate.

Plasticizers are used to adjust the film forming properties of the elastomer. Examples of suitable plasticizers include aliphatic hydrocarbon oils, e.g., naphthenic and paraffinic oils; liquid polydienes, e.g., liquid polybutadiene; and liquid

8

polyisoprene. Generally, plasticizers are liquids having molecular weights of less than about 5000, but can have molecular weights up to about 30,000. Plasticizers having low molecular weight will encompass molecular weights less than about 30,000.

Flexographic printing plates formed from photopolymerizable compositions which are soluble, swellable, or dispersible in aqueous, semi-aqueous, or organic solvent developers (so called wet development) may also be suitable for use in the present invention to the extent that the photopolymerizable composition is also capable of liquifying upon thermal development to form a relief surface. Examples of suitable compositions for solvent development have been disclosed, for example, in Chen et al., U.S. Pat. No. 4,323,637, Grüetzmacher et al., U.S. Pat. No. 4,427,749 and Feinberg et al., U.S. Pat. No. 4,894,315.

The thickness of the photopolymerizable layer can vary over a wide range depending upon the type of printing plate desired, for example, from about 0.010 inches to about 0.250 inches or greater (about 0.025 cm to about 0.64 cm or greater). For so-called "thin plates" typically the photopolymerization layer can range from about 0.010 inches to about 0.067 inches (about 0.025 cm to about 0.17 cm) in thickness.

The support can be any flexible material that is conventionally used with photosensitive elements used to prepare flexographic printing plates. Preferably the support is transparent to actinic radiation to accommodate "backflash" exposure through the support. Examples of suitable support materials include polymeric films such those formed by addition polymers and linear condensation polymers, transparent foams and fabrics. Under certain end-use conditions, metals such as aluminum, may also be used as a support, even though a metal support is not transparent to radiation. A preferred support is a polyester film; particularly preferred is polyethylene terephthalate. The support may be in sheet form or in cylindrical form, such as a sleeve. The sleeve may be formed from single layer or multiple layers of flexible material. Flexible sleeves made of polymeric films are preferred, as they typically are transparent to ultraviolet radiation and thereby accommodate backflash exposure for building a floor in the cylindrical printing element. Multiple layered sleeves may include an adhesive layer or tape between the layers of flexible material. Preferred is a multiple layered sleeve as disclosed in U.S. Pat. No. 5,301,610. The sleeve may also be made of non-transparent, actinic radiation blocking materials, such as nickel or glass epoxy. The support typically has a thickness from 0.002 to 0.050 inch (0.0051 to 0.127 cm). A preferred thickness for the sheet form is 0.003 to 0.016 inch (0.0076 to 0.040 cm). The sleeve typically has a wall thickness from 10 to 80 mils (0.025 to 0.203 cm) or more. Preferred wall thickness for the cylinder form is 10 to 40 mils (0.025 to 0.10 cm).

Optionally, the element includes an adhesive layer between the support and the photopolymerizable layer, or a surface of the support that is adjacent the photopolymerizable layer has an adhesion promoting surface. The adhesive layer on the surface of the support can be a subbing layer of an adhesive material or primer or an anchor layer as disclosed in U.S. Pat. No. 2,760,863 to give strong adherence between the support and the photopolymerizable layer. The adhesive compositions disclosed in Burg, U.S. Pat. No. 3,036,913 are also effective. Alternatively, the surface of the support on which the photopolymerizable layer resides can be treated to promote adhesion between the support and the photopolymerizable layer, with flame-treatment or electron-treatment, e.g., corona-treated. Further, the adhesion of the

## US 6,773,859 B2

9

photopolymerizable layer to the support can be adjusted by exposing the element to actinic radiation through the support as disclosed by Feinberg et al. in U.S. Pat. No. 5,292,617.

The photopolymerizable layer itself can be prepared in many ways by admixing the binder, monomer, initiator, and other ingredients. It is preferred that the photopolymerizable mixture be formed into a hot melt and then calendered to the desired thickness. An extruder can be used to perform the functions of melting, mixing, deaerating and filtering the composition. The extruded mixture is then calendered between the support and a temporary coversheet. Alternatively, the photopolymerizable material can be placed between the support and the temporary coversheet in a mold. The layers of material are then pressed flat by the application of heat and/or pressure. Cylindrical seamless photopolymerizable elements may be prepared according to the method and apparatus disclosed by Cushner et al. in U.S. Pat. No. 5,798,019.

The photosensitive element includes at least one photopolymerizable layer that can be of a bi- or multi-layer construction. Further, the photosensitive element may include an elastomeric capping layer on the at least one photopolymerizable layer. The elastomeric capping layer should have an elastic modulus in the polymerized state not substantially less than the elastic modulus of the photopolymerizable layer in the exposed state. The composition of the elastomeric layer comprises an elastomeric polymeric binder, an optional second polymeric binder and optionally a nonmigratory dye or pigment. The elastomeric composition can also contain a monomer or monomers and a photoinitiating system. The elastomeric polymeric binder in the elastomeric composition is generally the same as or similar to the elastomeric binder present in the photopolymerizable layer. The elastomeric capping layer is typically part of a multilayer cover element that becomes part of the photosensitive printing element during calendering of the photopolymerizable layer. Such multilayer cover elements and compositions suitable as the elastomeric capping layer are disclosed in Gruetzmacher et al., U.S. Pat. No. 4,427,759 and U.S. Pat. No. 4,460,675. Although the elastomeric capping layer may not necessarily contain photoreactive components, the layer ultimately becomes photosensitive when in contact with the photopolymerizable layer. As such, upon imagewise exposure to actinic radiation, the elastomeric capping layer has portions in which polymerization or crosslinking have occurred and portions which remain unpolymerized, i.e., uncrosslinked. Thermal treating at the developing temperature causes the unpolymerized portions of the elastomeric capping layer to soften or melt or flow along with the photopolymerizable layer, in order to form the relief surface. The elastomeric capping layer that has been exposed to actinic radiation remains on the surface of the polymerized areas of the photopolymerizable layer and becomes the actual printing surface of the printing plate.

The photosensitive element includes at least one thermally removable layer on the photopolymerizable layer. Depending on desired use, the thermally removable layer may be opaque or transparent to actinic radiation. The at least one thermally removable layer may have one or more functions for the photosensitive element including, but not limited to, a release layer, an actinic radiation opaque layer, a barrier layer (typically in conjunction with the actinic radiation opaque layer), an adhesion modifying layer, and a layer which alters the surface characteristics of the photosensitive element. The thermally removable layer should be substantially insensitive to the radiation that induces photoreaction in the photopolymerizable layer, which typically is ultraviolet radiation.

10

The primary purposes of a release layer are for ease in placing and removing an image-bearing transparency onto and from the photopolymerizable surface after exposure in a vacuum frame. (An image-bearing transparency may also be referred to herein as a mask, target, silver halide target, and phototool.) The release layer provides a substantially non-tacky surface to the typically tacky surface of the photopolymerizable layer. The release layer can also protect the surface of the photopolymerizable layer from being damaged during removal of an optional temporary coversheet and can ensure that the photopolymerizable layer does not stick to the coversheet. When the thermally removable layer is functioning as a release layer, the layer is transparent or substantially transparent, i.e., insensitive or substantially insensitive, to actinic radiation. A transparent or substantially transparent layer is one that permits all or at least a significant portion of the transmitted amount of actinic radiation to the underlying photopolymerizable layer so that a significant amount of photoinduced reaction occurs in the photopolymerizable layer. The thermally removable layer is also substantially transparent to actinic radiation when acting as an adhesion modifying layer and when altering the surface characteristics, such as surface roughness, ink pickup, or ink release properties of the photosensitive element. A sufficiently roughened exterior surface of the photosensitive element can eliminate the need for matte agent in films that are used as phototools (i.e., transparency mask). The matte agent in the phototool assures intimate contact between the phototool and the element upon exposure in vacuum.

When the thermally removable layer is the actinic radiation opaque layer, the layer is opaque or substantially opaque to actinic radiation. An opaque or substantially opaque layer is one in which the amount of actinic radiation transmitted to the underlying photopolymerizable layer is so minuscule that no significant amount of photoinduced reaction occurs in the photopolymerizable layer. When acting as the actinic radiation opaque layer, the thermally removable layer may completely cover or only partially cover the underlying photopolymerizable layer for the photosensitive element prior to the imagewise exposure step. If the actinic radiation opaque layer completely covers the underlying photopolymerizable layer, the actinic radiation opaque layer is first removed imagewise from the photosensitive element to uncover the photopolymerizable layer. The thermally removable layer as the radiation opaque layer forms the in situ mask on the photosensitive element for imagewise exposure of the photopolymerizable layer. The actinic radiation opaque layer typically is also sensitive to infrared radiation that is used to form the in situ mask. The in situ mask of the radiation opaque layer may be formed by any method including imagewise ablation of the radiation opaque layer by infrared laser radiation from the photosensitive element, imagewise transfer of the radiation opaque layer by infrared laser radiation from a donor element to the photosensitive element, imagewise adhesion balance change by infrared laser radiation between a substrate and the photosensitive element and inkjet application methods. It is possible to use more than one layer (thermally removable) to form the actinic radiation opaque layer. When the thermally removable layer is the actinic radiation opaque layer, the opaque areas should have a transmission optical density (visual filter) of greater than 2.0 in order to effectively block actinic radiation and the polymerization of the underlying photopolymerizable layer. The in situ mask remains on the photopolymerizable layer after imagewise exposure, and is removed during thermal treating.

## US 6,773,859 B2

## 11

The thickness of the thermally removable layer should be in the range suitable for its intended purpose. When the thermally removable layer is acting as the release layer, the thickness is less than 25 micron, preferably less than 15 microns. When the thermally removable layer is acting as the radiation opaque layer, the thickness should be in a range to optimize both sensitivity and opacity, which is generally from about 20 Angstroms to about 50 micrometers, preferably 20 Angstroms to 25 micrometers. For photosensitive elements having more than one thermally removable layer, the total thickness of the layers should be as thin as possible, that is, less than 75 microns, preferably less than 50 microns.

The thermally removable layer is selected from the group consisting of (a) an actinic radiation opaque layer comprising (i) at least one infrared absorbing material, (ii) a radiation opaque material, wherein (i) and (ii) can be the same or different, and at least one binder having a softening or melting temperature less than 190° C.; (b) a layer of a composition comprising at least one binder and filler agent, wherein the binder is less than 49% by weight based on the total weight of the binder and filler agent, and (c) a layer of particulate material having particle size of less than 23 micrometers. Depending upon the selection of materials used in the thermally removable layer (b) and (c), the thermally removable layer may function as a release layer, protective layer, surface altering layer, adhesion modifying layer, or as a digitally imageable layer, i.e., an actinic radiation opaque layer.

The thermally removable layer of the group (a) is an actinic radiation opaque layer comprising (i) at least one infrared absorbing material, (ii) a radiation opaque material, wherein (i) and (ii) can be the same or different, and at least one binder having a softening or melting temperature less than 190° C. The binder for the thermally removable layer (a) is at least 51% by weight, based on the total weight of binder, the radiation opaque material and the infrared absorbing material. Since the binder is present in greater proportion than the radiation opaque material and/or the infrared absorbing material, the thermally removable layer (a) forms a continuous film disposed above the photopolymerizable layer.

To the extent that the following binders have a softening or melting temperature less than 190° C., the binders which are suitable for use in the actinic radiation opaque layer (a) include, but not limited to, polyamides, polyethylene oxide, polypropylene oxide, ethylcellulose, hydroxyethyl cellulose, cellulose acetate butyrate, ethylene-propylene-diene terpolymers, copolymers of ethylene and vinyl acetate, copolymers of vinyl acetate and vinyl alcohol, copolymers of vinyl acetate and pyrrolidone, polyvinyl acetate, polyethylene wax, polyacetal, polybutyral, polyalkylene, polycarbonates, polyester elastomer, copolymers of vinyl chloride and vinyl acetate, copolymers of styrene and butadiene, copolymers of styrene and isoprene, thermoplastic block copolymers of styrene and butadiene, thermoplastic block copolymers of styrene and isoprene, polyisobutylene, polybutadiene, polycholorprene, butyl rubber, nitrile rubber, thermoplastic polyurethane elastomer, cyclic rubbers, copolymers of vinylacetate and (meth)acrylate, acrylonitrile-butadiene-styrene terpolymer, methacrylate-butadiene-styrene terpolymer, alkyl methacrylate polymer or copolymer, copolymers of styrene and maleic anhydride, copolymers of styrene and maleic anhydride partially esterified with alcohols, and combinations thereof. Some of the above materials, particularly the copolymeric elastomeric compounds do not have a actual softening or melting point, but rather transition from a

## 12

viscous or rubbery condition to a hard relatively brittle condition which is expressed as a glass transition temperature, Tg. Preferred binders having a softening or melting temperature less than 190° C. include polyamides, polyethylene oxide, polypropylene oxide, ethylcellulose, hydroxyethyl cellulose, cellulose acetate butyrate, ethylene-propylene-diene terpolymers, copolymers of ethylene and vinyl acetate, copolymers of vinyl acetate and vinyl alcohol, copolymers of vinyl acetate and pyrrolidone, polyvinyl acetate, polyethylene wax, polyacetal, polybutyral, polyalkylene, polycarbonates, cyclic rubber, copolymer of styrene and maleic anhydride, copolymer of styrene and maleic anhydride partially esterified with alcohol, polyester elastomers, and combinations thereof.

Materials suitable for use as the radiation opaque material and the infrared absorbing material include, but is not limited to, metals, metal alloys, pigments, carbon black, graphite and combinations thereof. Mixtures of pigments in which each pigment functions as the infrared absorbing material, or the radiation opaque material (or both) can be used with the binder. Dyes are also suitable as infrared absorbing agents. Examples of suitable dyes include poly(substituted)phthalocyanine compounds; cyanine dyes; squarylium dyes; chalcogenopyrroarylidene dyes; bis(chalcogenopyrrolo)-polymethine dyes; oxyindolizine dyes; bis(aminoaryl)-polymethine dyes; merocyanine dyes; croconium dyes; metal thiolate dyes; and quinoid dyes. Preferred is carbon black, graphite, metal, and metal alloys that functions as both the infrared absorbing material and the radiation opaque material. The radiation opaque material and the infrared absorbing material may be in dispersion as described below to facilitate handling and uniform distribution of the material. Typically, the radiation opaque material and the infrared absorbing materials have melting temperatures above the treating temperature.

The thermally removable layer of the group (b) is a layer of a composition comprising at least one binder and filler, wherein the binder is less than 49% by weight based on the total weight of the binder and filler. The binder for the thermally removable layer can be from 1 to 49% by weight, based on the total weight. Since the amount of binder in the thermally removable layer (b) is less than 49% by weight, the filler is present at least 51% by weight based on the total amount of binder and filler in the layer (b). The filler in the thermally removable layer (b) of at least 51% by weight forms a discontinuous layer with the binder. The thermally removable layer (b) being a discontinuous layer is particularly useful when the binder for layer (b) has a melting point or softening point above 190° C. During thermal treatment, the application of heat and contacting with the absorbent material, preferably with added pressure, aids in the formation of microcracks in the discontinuous layer so that the thermally removable layer and the underlying unpolymerized portions of the photopolymerizable layer can be thoroughly removed during treatment. Microcracks are breaks, fractures, or cracks which are small, that is, on the order of microns or significantly less in size. The filler, or an inorganic dispersion of the filler, will not form a film by itself. Generally, a binder alone is capable of forming a film. But when the binder has a melting or softening temperature above the treating temperature (i.e., greater than 200° C.) and forms a continuous layer with a filler (that is, the binder is in a greater proportion to the filler) on the photopolymerizable layer, the layer does not melt, soften, or flow during thermal treating and results in incomplete removal of the resulting layer and/or the unpolymerized portions. Binders having a melting point or softening point below 190° C. are

## US 6,773,859 B2

13

also suitable for use in the thermally removable layer (b). Thus, the melting point or softening point of a material or materials in a layer disposed above the photopolymerizable layer is not longer a limitation of a photosensitive element for use in a thermal development process. (See Examples 7 and 8.) It is also possible to include one or more additional binders with the binder of thermally removable layer (b). The coating thickness of the thermally removable layer (b) should be less than 50 micrometers, preferably less than 25 micrometers.

Binders suitable for use in the thermally removable layer (b) include, but are not limited to, polyvinyl alcohol, poly(meth)acrylic acids, metal alkali salts of poly(meth)acrylic acids, amphoteric interpolymers, hydroxyalkyl cellulose, cellulose acetate, nitrocellulose, polyimides, polyesters, polyphenylene ethers, polyacrylonitrile, polystyrene, copolymers of styrene and methacrylic acid, polyvinyl chloride, polyesters, polyacrylamide, copolymers of imides and amides, polychlorotrifluoroethylene, ethylene and chlorotrifluoroethylene copolymer, polytetrafluoroethylene, copolymers of ethylene and tetrafluoroethylene copolymer, polyether ether ketone, polybenzimidazoles, copolymers of vinylidene fluoride and hexafluoropropylene, and combinations thereof. The binders recited above for the thermally removable layer (a) are also suitable as binders for the thermally removable layer (b).

A dispersant is generally added when a pigment or a filler is present in order to disperse the fine particles and avoid flocculation and agglomeration. A wide range of dispersants is available. Suitable dispersants are the A-B dispersants generally described in "Use of A-B Block Polymers as Dispersants for Non-Aqueous Coating Systems" by H. K. Jakubauskas, *Journal of Coating Technology*, Vol. 58, Number 736, pages 71-82. Useful A-B dispersants are disclosed in U.S. Pat. Nos. 3,684,771; 3,788,996; 4,070,388, and 4,032,698. The dispersant is generally present in the thermally removable layer in an amount of 0.1 to 20% by weight, based on the total weight of the layer. But, the amount of dispersant for the filler is not included when determining the weight percentage of the binder or the filler in the thermally removable layer (b).

The filler can have color or be colorless. If the filler has color, it is preferred that the thermally removable layer (b) should be opaque to actinic radiation. Materials suitable for use as the filler include mineral fillers, such as, calcium carbonate, kaolin, feldspar, synthetic silica, natural silica, talc, silicon carbide, aluminum oxides, beryllium oxide, iron oxide, lead oxide, magnesium oxide, titanium oxide, zinc oxide, zirconium oxide, glass with or without surface treatment, sulfates, sulfides, silicates and titanates; metallic fillers, such as iron, steel, aluminum, copper, nickel, silver, zinc, lead, metallized glass; metallic alloys, such as, zinc and copper; flame retardants, such as, antimony oxide, alumina trihydrate, phosphorus; organic fillers, such as woodflour, starches and synthetic materials such as crosslinked particles of polymethylmethacrylate; carbon black; graphite; pigments; and combinations thereof. Fillers may also function as infrared absorbing materials and uv absorbing materials. Preferred are carbon black, graphite, silica, metallic fillers, metal alloys, pigments, and crosslinked organic fillers. It is preferred to use a filler having fine particle size which is in dispersion. The particle size of the filler is less than 23 micrometers, and preferably less than 17 micrometers. The shape of the particles of filler is not limited.

Other additives, such as dispersants, surfactants, rheology modifiers, may also be present in the thermally removable layers (a) and (b).

14

The thermally removable layer of the group (c) is a layer of particulate material having particle size of less than 23 micrometers. The particulate material is a fine powder of particles in which at least 90 percent by volume of the particulate material has a particle size of an equivalent spherical diameter of less than 23 micrometers. It is preferred that at least 50 percent by volume of the particulate material has a particle size of an equivalent spherical diameter of less than 17 micrometers.

For the purpose of determining particle size of the particulate material for layer (c) as well as the filler for layer (b), particles are measured with a Coulter® Multisizer instrument, Coulter Electronics, Inc., Hialeah, Fla. The term particle size as used herein with respect to the particulate material and filler covers the size distribution of the smallest, independently acting unit. The particle size is based upon an equivalent spherical diameter of each particle. The size of particles suitable for use as the particulate material in the thermally removable layer (c) and the filler for layer (b) is less than 23 microns (micrometers), and preferably less than 17 micrometers. Based on a volumetric distribution of particulate material sampled, at least 90% of the particulate material must have a particle size of less than 23 microns, and at least 50% of the particulate material must have a particle size less than 17 microns. The shape of the particles of the particulate material is not limited.

The surface of the photopolymerizable layer opposite the support is an exterior surface which is tacky or substantially tacky, i.e., be sticky or have an oiliness to the touch of the surface of the layer. The exterior surface should be tacky enough to secure an overall layer of particulate material on the surface of the element. Typically, the surface of the photopolymerizable layer is inherently tacky due to the elastomeric binder and/or to migratory compounds, such as monomer and plasticizer, in the photopolymerizable layer. In most cases, the particulate material will be applied directly to the photopolymerizable layer since the photopolymerizable layer is tacky and will adhere the particulate material to the element. If more than one photopolymerizable layer is present in the element, the exterior surface of the outermost layer must be tacky or substantially tacky. After application of the particulate material to the tacky exterior surface of the photopolymerizable layer, the surface or a portion of the surface is rendered tack-free or substantially tack-free. The layer of particulate material may be a monolayer or multiple layers to render the exterior surface tack-free. The thermally removable layer (c) of particulate material may entirely cover or partially cover the photopolymerizable layer. The particulate material can be colorless to form a transparent or substantially transparent layer on the photosensitive element. Alternately, the particulate material can be colored which includes black, to form the actinic radiation opaque layer on the element.

The particulate material can be organic, inorganic, metallic, metallic alloys, pigments, carbon black, graphite, mixtures of organic and inorganic compounds, or multicomponent. Materials suitable for use as the particulate material include, but are not limited to, polyethylene powders; polytetrafluoroethylene powders; diatomaceous silicas; cellulose acetates; polyvinyl alcohol powders; matte agents, such as, silica, rice starch, and polymethylmethacrylate powders; and inorganic particles, such as, titanium dioxide, zinc oxide, magnesium oxide, and alumina. Additional materials suitable for use as the particulate material are pigment particles; toner particles; mixtures of pigment particles; mixtures of toner particles; and mixtures of pigment and toner particles. Non-limiting examples of pigment particles include carbon

## US 6,773,859 B2

15

black; graphite; copper chromite; chromium oxides; cobalt chrome aluminate; metals, such as, aluminum, copper, and zinc; and metal alloys of bismuth, indium, zinc, and copper. Toner particles are pigmented organic resin particles that comprise pigment particles finely dispersed in a resin matrix that is then ground to the desired size.

Suitable resin matrices for the toners include, but are not limited to, polyamides, polyethylene oxide, polypropylene oxide, ethylcellulose, hydroxyethyl cellulose, cellulose acetate butyrate, ethylene-propylene-diene terpolymer, copolymers of ethylene and vinyl acetate, copolymers of vinyl acetate and vinyl alcohol, copolymers of vinyl acetate and pyrrolidone, polyvinyl acetate, polyethylene wax, polyacetal, polybutyral, polyalkylene, polycarbonates, polyester elastomer, copolymers of vinyl chloride and vinyl acetate, cyclic rubbers, copolymers of vinylacetate and (meth)acrylate, acrylonitrile-butadiene-styrene terpolymer, methacrylate-butadiene-styrene terpolymer, alkyl methacrylate polymer or copolymer, copolymers of styrene and maleic anhydride, copolymers of styrene and maleic anhydride partially esterified with alcohols, polyvinyl alcohol, poly(meth)acrylic acids, metal alkali salt of poly(meth)acrylic acids, amphoteric interpolymers, cellulose acetate, nitrocellulose, polyimides, polyesters, polyphenylene ethers, polyacrylonitrile, polystyrene, copolymers of styrene and methacrylic acid, polyvinyl chloride, polyacrylamide, copolymers of imides and amides, polychlorotrifluoroethylene, ethylene and chlorotrifluoroethylene copolymer, polytetrafluoroethylene, copolymers of ethylene and tetrafluoroethylene, polyether ether ketone, polybenzimidazoles, copolymers of vinylidene fluoride-hexafluoropropylene copolymer and mixtures thereof. Preferred resin matrices are polyvinyl chloride, cellulose acetate, cellulose acetate butyrate, polystyrene, polymethyl methacrylate, polyvinyl alcohol, methyl cellulose, and carboxymethyl cellulose. Particulate materials may be dispersed with wetting agents, dispersants, extenders, softeners, and other adjuvants to adjust particle size and to facilitate handling or in the process of use. The surface of the particulate material may be modified with for example, antistatic agents and slip agents, to provide particles with desired characteristics. Particle size may be adjusted to attain the desired particle size by, for example, milling.

Particularly preferred toners are toners sold by DuPont as Cromalin® black toners, for example, Cromalin® type KK6 black toner which is carbon black and cellulose acetate blend. Particularly preferred particulate materials for forming a radiation opaque layer are carbon black, graphite, mixtures of pigments, toners containing carbon black, metals and metal alloys, such as copper, zinc, and aluminum, and a mixture thereof.

The particulate material can include additives to improve covering power and uniform application of the particulate material as a layer. The particulate material may be dispersed with wetting aids, surfactants, extenders, softeners, and other adjuvants to adjust particle size and to facilitate handling or in the process of use. The surface of the particles of particulate material can be modified with for example, antistatic agents and slip agents, to provide the particles with desired characteristics.

When the particulate material is applied to the photopolymerizable layer it imparts a dry, non-tacky finish to the surface of the photosensitive element. The particulate material can be applied to the surface of the photosensitive element opposite the support by any method including, hand dusting or by mechanical means, such as applicators and automated toning machines, with dry powder, and powder

16

coating. Hand application is usually accomplished by dipping a pad of tufted material into a tray of particulate material, applying the particulate material in excess and wiping the pad over the entire surface of the photosensitive element. Excess material is then wiped off. The particulate material may also be applied from a liquid dispersion.

It was surprising to find that the particulate materials in the thermally removable layer (c) can be successfully thermally processed regardless of the class of material and the melting point of the material (see Examples 3, 4, 5, 6, and 13). The size of the particle of the particulate material is important since particle size influences the ease of removal of the particulate from fine reverses in the relief, and the degree of packing of the particles on the layer (see Examples 6 and 13).

Further particle size is also particularly critical when the layer (c) functions as an actinic radiation opaque layer. The particle size affects the toned density, i.e., degree of packing, and actinic radiation blocking capability of the layer (c). It is also possible to use more than one thermally removable layers or types of thermally removable layers. The exact choice of additional layer(s) will depend on the nature of the photopolymerizable layer, the function of the thermally removable layer, and other physical requirements of the photosensitive element. For example, a second thermally removable layer as defined above may be necessary between the photopolymerizable layer and the thermally removable layer acting as a radiation opaque layer. The second thermally removable layer can act as a barrier layer to protect the integrity of the radiation opaque layer from the migratory materials, such as monomers, plasticizers, and initiators, in the photopolymerizable layer. In such instances, the infrared sensitivity and the handling properties of the thermally removable layer may be altered. In addition, such migration can cause smearing and tackifying of the infrared-sensitive layer after imaging. Additionally, if migratory materials migrated to the thermally removable layer, photocrosslinking in the UV exposed areas of the thermally removable layer may occur and would detrimentally impact the thermal processability of the thermally removable layer. The migration of monomer and/or plasticizer can also reduce the degree of photopolymerization of the exposed areas and reduce the thermal development (removal) capabilities in the unexposed areas of the photopolymerizable layer. Also, migration of materials to the thermally removable layer may adversely impact the adhesion balance between the thermally removable layer and the photopolymerizable layer such that the coversheet of the second element (supporting the thermally removable layer) may not be removable.

The thermally removable layer may be formed above or on the surface of the photopolymerizable layer opposite the support by any method including, coated directly onto the surface of the photopolymerizable layer, or coated separately onto a temporary support or the coversheet and transferred to the surface of the photopolymerizable layer, or formed as a layer of the multilayer cover element which then becomes an assemblage with the photosensitive element, or particulate material toned or applied or transferred to the photopolymerizable layer.

The photosensitive printing element of the present invention may further include a temporary coversheet on top of the uppermost layer of the photosensitive element, that is, the thermally removable layer. One purpose of the coversheet is to protect the uppermost layer of the photosensitive printing element during storage and handling. Examples of suitable materials for the coversheet include thin films of polystyrene, polyethylene, polypropylene, polycarbonate,

## US 6,773,859 B2

17

fluoropolymers, polyamide or polyesters, which can be subbed with release layers. The coversheet is preferably prepared from polyester, such as Mylar® polyethylene terephthalate film; most preferably the coversheet is 5-mil Mylar®.

In preparation for the next step of the process which is to overall expose the photosensitive element to actinic radiation through a mask, a mask image may need to be formed on or disposed above the surface of the photopolymerizable layer opposite the support. The mask includes opaque areas and "clear" areas that form the image. The opaque areas of the mask prevent the photopolymerizable material beneath from being exposed to the radiation and hence those areas of the photopolymerizable layer covered by the dark areas do not polymerize. The "clear" areas of the mask expose the photopolymerizable layer to actinic radiation and polymerize or crosslink. The image necessary for the imagewise exposure of the photopolymerizable layer can be generated by any method including conventional and digital methods, including inkjet application.

Digital methods create a mask image in situ on or disposed above the photopolymerizable layer with laser radiation. Any of the thermally removable layers (a), (b), and (c), which is capable of blocking actinic radiation can be used to form the in situ mask image. Digital methods of creating the mask image require one or more steps to prepare the photosensitive element prior to imagewise exposure. Generally, digital methods of in situ mask formation either selectively remove or transfer the radiation opaque layer, from or to a surface of the photosensitive element opposite the support. It is preferred that the thermally removable layer acting as a radiation opaque layer is also sensitive to infrared radiation in order to carry out the digital methods for forming the mask image with the preferred infrared laser radiation. The presence of materials that are black, such as dark inorganic pigments, such as carbon black and graphite, mixtures of pigments, metals, and metal alloys function as both infrared-sensitive material and radiation-opaque material. The infrared laser exposure can be carried out using various types of infrared lasers, which emit in the range 750 to 20,000 nm. Infrared lasers including, diode lasers emitting in the range 780 to 2,000 nm and Nd:YAG lasers emitting at 1064 nm are preferred. If the color of the powder material is other than black (and not transparent), the wavelength of the laser radiation which forms the in situ mask should be selected so as to be absorbent to the color of the layer and not initiate photoreaction in the laser exposed photopolymerizable layer. The in situ mask images remain on the photosensitive element for subsequent steps of overall exposure to actinic radiation and thermal treating.

In one digital method, the photosensitive element will initially include the thermally removable layer as a radiation opaque layer that covers or substantially covers the entire surface of the photopolymerizable layer. The radiation opaque layer is exposed imagewise to infrared laser radiation to form the image on or disposed above the photopolymerizable layer, i.e., the in situ mask. The infrared laser radiation can selectively remove, e.g., ablate or vaporize, the infrared sensitive layer (i.e., radiation opaque layer) from the photopolymerizable layer, as disclosed by Fan in U.S. Pat. Nos. 5,262,275 and 5,719,009; and Fan in EP 0 741 330 B1. A material capture sheet adjacent the radiation opaque layer may be present during laser exposure to capture the material as it is removed from the photosensitive element as disclosed by Van Zoeren in U.S. Pat. No. 5,506,086. Only the portions of the radiation opaque layer that were not removed from the photosensitive element will remain on the element

18

forming the in situ mask and will become the thermally removable layer for thermal treating.

In another digital method of mask formation, the photosensitive element will not initially include the thermally removable layer. A separate element bearing the thermally removable layer as a radiation opaque layer will form an assemblage with the photosensitive element such that the radiation opaque layer is adjacent the surface of the photosensitive element opposite the support, which is typically the photopolymerizable layer. (If present, a coversheet associated with the photopolymerizable layer is removed prior to forming the assemblage). The separate element may include one or more other layers, such as ejection layers or heating layers, to aid in the digital exposure process. Hereto, the radiation opaque layer is also sensitive to infrared radiation. The assemblage is exposed imagewise with infrared laser radiation to selectively transfer the radiation opaque layer and form the image on or disposed above the photopolymerizable layer as disclosed by Fan et al. in U.S. Pat. No. 5,607,814; and Blanchett in U.S. Pat. Nos. 5,766,819; 5,840,463; and EP 0 891 877 A. Only the portions of the radiation opaque layer which were transferred will reside on the photosensitive element forming the in situ mask and will be the thermally removable layer for thermal treating.

Further, the mask image may be created on a separate carrier and then transferred by application of heat and/or pressure to the surface of the photopolymerizable layer opposite the support. The photopolymerizable layer is typically tacky and will retain the transferred image. The separate carrier can then be removed from the element prior to imagewise exposure. The separate carrier may have a radiation opaque layer that is imagewise exposed to laser radiation to selectively remove the radiation opaque material and form the image. An example of this type of carrier is LaserMask® imaging film by Rexam, Inc. Alternatively, the image of radiation opaque material may be transferred to the separate carrier from another element having the radiation opaque material by laser radiation.

It is also contemplated that digital mask formation can be accomplished by imagewise application of the radiation opaque material in the form of inkjet inks. Inkjet inks may be formulated according to the description above for any of the thermally removable layers (a), (b), and (c). Imagewise application of an ink-jet ink can be directly on the photopolymerizable layer or disposed above the photopolymerizable layer on another thermally removable layer, e.g., transparent layer, of the photosensitive element. (See Example 10)

The next step of the process of the present invention is to overall expose the photosensitive element to actinic radiation through a mask, that is, imagewise exposure of the element. If the digital mask was formed in situ on the photosensitive element, the element is overall exposed through the in situ mask image.

Alternatively, a conventional method for imagewise exposure is by using an image-bearing transparency film or phototool, typically a silver halide film, as the mask. Typically, the phototool includes the image on a polyester base that is 5 to 7 mils thick. The image-bearing transparency film is placed on the thermally removable layer the functions as a release layer, a vacuum is pulled to assure good contact of the mask film to the element, and the element is exposed. The image-bearing transparency film is removed from the element prior to thermal treating. Similarly, a template having at least actinic radiation blocking portions can be disposed above the photopolymerizable

## US 6,773,859 B2

19

layer of the photosensitive element before the element is exposed. The template is removed from the element prior to thermal processing.

In use, the photosensitive element of the present invention is exposed to actinic radiation from suitable sources. The actinic radiation exposure time can vary from a few seconds to minutes, depending upon the intensity and spectral energy distribution of the radiation, its distance from the photosensitive element, the desired image resolution, and the nature and amount of the photopolymerizable composition. Exposure temperatures are preferably ambient or slightly higher, i.e., about 200 to about 35° C. Exposure is of sufficient duration to crosslink the exposed areas down to the support or to the back exposed layer. Imagewise exposure time is typically much longer than backflash exposure time, and ranges from a few to tens of minutes.

Actinic radiation sources encompass the ultraviolet and visible wavelength regions. The suitability of a particular actinic radiation source is governed by the photosensitivity of the initiator and the at least one monomer used in preparing the flexographic printing plates. The preferred photosensitivity of most common flexographic printing plates are in the UV and deep UV area of the spectrum, as they afford better room-light stability. Examples of suitable visible and UV sources include carbon arcs, mercury-vapor arcs, fluorescent lamps, electron flash units, electron beam units, lasers, and photographic flood lamps. The most suitable sources of UV radiation are the mercury vapor lamps, particularly the sun lamps. Examples of industry standard radiation sources include the Sylvania 350 Blacklight fluorescent lamp (FR48T12/350 VL/VHO/180, 115 w), and the Philips UV-A "TL"-series low-pressure mercury-vapor fluorescent lamps. Typically, a mercury vapor arc or a sunlamp can be used at a distance of about 1.5 to about 60 inches (about 3.8 to about 153 cm) from the photosensitive element. These radiation sources generally emit long-wave UV radiation between 310–400 nm. Flexographic printing plates sensitive to these particular UV sources use initiators that absorb between 310–400 nm, and a suitable photobleachable compound should be absorptive in at least a portion of the 310–400 nm spectral range.

Imagewise exposure of the photosensitive element to actinic radiation may be conducted in the presence or absence of atmospheric oxygen for photosensitive elements having an in situ mask. Atmospheric oxygen is eliminated when the exposure is conducted in a vacuum. The exposure may be conducted in a vacuum to minimize the effects of oxygen on the polymerization reactions occurring in that layer. And for photosensitive elements that are exposed through an image transparency, the exposure must be conducted in vacuum to assure good contact between the image transparency and the photosensitive element. The exposure may be conducted in the presence of atmospheric oxygen since the mask is formed in situ or applied imagewise with radiation opaque material on the photopolymerizable layer, there is no need for vacuum to assure intimate contact. In the process of preparing a digital flexographic printing plate or sleeve, the overall exposure step preferably is conducted without vacuum, i.e., while the photosensitive element is in the presence of atmospheric oxygen, and without any additional layers present on top of the in situ mask.

A step change in printing performance was observed for a photosensitive element having an in situ mask was exposed in the presence of atmospheric oxygen and thermally treated relative to a photosensitive element that was given a conventional analog exposure and thermally treated as shown in Example 1. Further, imagewise exposure in the

20

presence of atmospheric oxygen for the photosensitive element provided improved processing latitude since fewer thermal cycles of heating and contacting with an absorbent material were needed to achieve the same relief depth and improved reverse depth as shown in Examples 1 and 12.

The process of the invention usually includes a back exposure or backflash step. This is a blanket exposure to actinic radiation through the support. It is used to create a layer of polymerized material, or a floor, on the support side of the photopolymerizable layer and to sensitize the photopolymerizable layer. The floor provides improved adhesion between the photopolymerizable layer and the support, helps highlight dot resolution and also establishes the depth of the plate relief. The backflash exposure can take place before, after or during the other imaging steps. It is preferred that it takes place after to the overall exposure to actinic radiation through the mask and prior to thermal treating. Any of the conventional radiation sources discussed above for the overall (imagewise) actinic radiation exposure step can be used for the backflash exposure step. Exposure time generally range from a few seconds up to a few minutes.

Following overall exposure to actinic radiation through the mask, the element is prepared for thermal development. If the mask is an image-bearing transparency film, i.e., phototool, or a template, the film or template is removed prior to treating the element. When digital methods were used to form the mask, the mask remains on the photosensitive element and is present during thermal treating.

The treating step removes at least the photopolymerizable layer in the areas which were not exposed to actinic radiation, i.e., the non-polymerized areas or uncured areas of the photopolymerizable layer. For photosensitive elements having a transparent thermally removable layer, i.e., release layer, surface modifying layer, or adhesion modifying layer, the thermal treating step shall also remove or substantially remove the thermally removable layer on the polymerized areas of the photopolymerizable layer from the photosensitive element. For photosensitive elements that the mask was formed digitally, the thermal treating step also removes the mask image (which had been exposed to actinic radiation) and the underlying unexposed areas of the photopolymerizable layer, as well as any other thermally removable layers which may be present.

The imagewise exposed photosensitive element is then ready for the next step of the present process which is thermally treating the exposed element to develop the relief image or pattern. Thermally treating the element includes heating the exposed photopolymerizable layer and the thermally removable layer at a temperature sufficient to cause the unexposed (uncured) portions of the element to soften or melt or flow, and contacting the layer to an absorbent surface to absorb the melt or flow portions. The polymerized areas of the photopolymerizable layer have a higher melting temperature than the unpolymerized areas and therefore do not melt, soften, or flow at the development temperatures. The term "melt" is used to describe the behavior of the unirradiated portions of the photopolymerizable elastomeric layer subjected to an elevated temperature that softens and reduces the viscosity to permit flow and absorption by the absorbent material. The material of the meltable portion of the photopolymerizable layer is usually a viscoelastic material which does not have a sharp transition between a solid and a liquid, so the process functions to absorb the heated composition layer at any temperature above some threshold for absorption in the absorbent material. A wide temperature range may be utilized to "melt" the composition layer for the purposes of this invention. Absorption may be slower at

## US 6,773,859 B2

21

lower temperatures and faster at higher temperatures during successful operation of the process.

The thermal treating steps of heating the photopolymerizable layer and the thermally removable layer and contacting the layer/s with an absorbent material can be done at the same time, or in sequence provided that the uncured portions of the photopolymerizable layer are still soft or in a melt state when contacted with the absorbent material. The photopolymerizable layer and the thermally removable layer/s are heated by conduction, convection, radiation, or other heating methods to a temperature sufficient to effect melting of the uncured portions but not so high as to effect distortion of the cured portions of the layer. The photosensitive element is heated to a surface temperature above about 40° C.; preferably from about 40° C. to about 230° C. (104–446° F.), more preferably from about 100 to 200° C., and most preferably from 100 to 160° C. in order to effect melting or flowing of the uncured portions of the photopolymerizable layer and the thermally removable layer. The absorbent material contacts the surface of the heated photosensitive element, and absorbs the softened or molten or flowing portions of the elastomeric layer from the unirradiated portions, forming a flexographic printing plate in which the uncured portions are removed to form a relief pattern or surface. The thermally removable layer disposed above the photopolymerizable layer may soften or melt or flow and be absorbed as well by the absorbent material. The thermally removable layer disposed above the photopolymerizable layer may form microcracks as a result of the contacting with the absorbent material and thus may be carried by the softened or molten or flowing portions of the photopolymerizable layer to the absorbent material. By maintaining more or less intimate contact of the absorbent material with the photopolymerizable layer that is molten in the uncured regions and the thermally removable layer, a transfer of the uncured photosensitive material from the photopolymerizable layer to the absorbent material takes place. While still in the heated condition, the absorbent material is separated from the cured photopolymerizable layer in contact with the support layer to reveal the relief structure. A cycle of the steps of heating the photopolymerizable elastomeric layer and contacting the molten (portions) layer with an absorbent material can be repeated as many times as necessary to adequately remove the uncured material and create sufficient relief depth. However, it is desirable to minimize the number of cycles for suitable system performance, typically the photopolymerizable element is thermally treated for 5 to 15 cycles.

A preferred apparatus to thermally develop the photosensitive element is disclosed by Peterson et al. in U.S. Pat. No. 5,279,697, and also by Johnson et al. in Patent Cooperation Treaty Application No. PCT/US00/24400 filed Sep. 6, 2000 (IM-1289 PCT). The photosensitive element may be placed on a drum or a planar surface in order for thermal treatment to be carried out.

The absorbent material is selected having a melt temperature exceeding the melt temperature of the unirradiated or uncured portions of the radiation curable composition and having good tear resistance at the same operating temperatures. Preferably, the selected material withstands temperatures required to process the photosensitive element during heating. The absorbent material is selected from non-woven materials, paper stocks, fibrous woven material, open-celled foam materials, porous materials that contain more or less a substantial fraction of their included volume as void volume. The absorbent material can be in web or sheet form. Preferred absorbent materials utilized to remove or wick away

22

the uncured portions of the photopolymerizable layer from the cured portions of the layer are selected from absorbent materials which possess internal strength and tear resistance to temperatures up to, including and slightly beyond the melting temperature of the uncured photopolymerizable material. The absorbent materials should also possess a high absorbency for the molten elastomeric composition as measured by the grams of elastomer that can be absorbed per square millimeter of the absorbent material. Preferred is a non-woven nylon web.

Intimate contact of the absorbent material to the photopolymerizable layer (while in the uncured portions are melt) may be maintained by the pressing the layer and the absorbent material together. It is desirable to apply a substantially uniform pressure of between about 2.11 kilograms per square centimeter and about 4.92 kilograms per square centimeter, with a preferred pressure of about 3.16 kilograms per square centimeter during processing. Pressure is applied to force the absorbent material into intimate contact with the photopolymerizable layer. It is believed that between about 0.70 kilograms per square centimeter and about 7.03 kilograms per square centimeter in a nip of the area in contact is adequate to enhance the absorption from the layer surface to the absorbent material without distorting the relief features on the photosensitive element. It is particularly preferred for photosensitive elements having a thermally removable layer (b) or (c) to apply pressure with contacting of the absorbent material. The application of pressure causes microcracks in the thermally removable layer/s to form which allow unpolymerized portions of the photopolymerizable layer to flow and carry away, i.e., remove, the materials of the thermally removable layer.

The photosensitive printing elements of the present invention can be uniformly post-exposed to ensure that the photopolymerization process is complete and that the element will remain stable during printing and storage. This post-exposure step can utilize the same radiation source as the main overall exposure.

Detackification is an optional post-development treatment that can be applied if the surface of the photosensitive printing element is still tacky, such tackiness not generally being removed in post-exposure. Tackiness can be eliminated by methods well known in the art, such as treatment with bromine or chlorine solutions. Preferably, detackification is accomplished by exposure to radiation sources having a wavelength not longer than 300 nm, as disclosed in European Published Patent Application 0 017927 and Gibson U.S. Pat. No. 4,806,506.

## EXAMPLES

In the following examples, all percentages are by weight unless otherwise noted. CYREL® photopolymer printing plates, CYREL® exposure unit, CYREL® Fast 1000 TD processor, CYREL® Digital Imager, CYREL® OPTISOL® developing solution are all available from The DuPont Company (Wilmington, Del.).

## Example 1

The following Example demonstrates the process of this invention of thermally treating a photosensitive element having a thermally removable layer which is actinic radiation opaque. The unexpected benefits in printing performance of the photosensitive element which is UV exposed in air and thermally processed are also shown.

Comparative and Control samples were prepared as follows. CYREL photopolymer plates, type HOS (67 mils)

## US 6,773,859 B2

23

were used. The plates included a photopolymerizable layer of a binder, at least one monomer, and photoinitiator, and a release layer of 80 wt. % of Macromelt® 6900 polyamide (from Henkel Corp.) and 20 wt. % of Amphomer® 28-4910 (a polymer from National Starch & Chemical Co. according to U.S. Pat. No. 3,927,199), and a coversheet. (The Macromelt polyamide binder has a softening point of 135° C. The melting point of the Amphomer binder is not available, but the glass transition temperature, T<sub>g</sub>, is 0.120° C. Since the T<sub>g</sub> for common polymers is typically 100 to 240° C. higher than the melting temperature as shown in data from *Polymer Handbook*, J. Brandup and F. H. Immergut, eds., Interscience, New York, 1966, it is estimated that the softening point for Material 2 is most likely at least 220° C.)

Three 67 HOS plates were given a back flash exposure of 12 seconds on a Kelleigh exposure unit. The coversheet was discarded. Three identical silver halide targets having 150 lines per inch screen ruling tonal range (2, 3, 4, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 95, 96, 97, 98 & 99 dots, and solid), slur targets, and fine positive and negative lines images were used during the main UV imaging step. The targets (with the silver halide emulsion down) were laid on the release layer surface the photopolymer plate and the vacuum was pulled to its maximum value with Kreen coversheet (5 mils thick) on top. Plates were exposed for 9 minutes on the same 2001 exposure unit. After removing from the vacuum frame, they were processed differently.

Two exposed plates, Comparative 1A and 1B, were thermally treated in a thermal processor similar to the processor described by Peterson et al. in U.S. Pat. No. 5,279,697. The processor used for this example was modified to include an infrared (IR) heater with a maximum power of 5200W to heat an outer surface of the plate. The processor further included cooling with air of the plate after separation of an absorbent material from the photopolymerizable layer. The absorbent material was CEREX non-woven nylon web type 2320. For this test, the IR heater was run at 30% of its maximum output, with drum speed of 30 inch/min (76.2 cm/minute). The temperature of the developer roll was 300° F. (148.9° C.). The temperature of the drum was set at 70° F. The pressure associated with contacting the plates to the absorbent material (drum to developer roll) was 30 psi on the cylinders. The cooling blower was on.

Plate samples for Comparatives 1A and 1B were processed for 6 cycles and 12 cycles of heating and contacting (with the absorbent material) respectively. The exposed plates were placed and clamped to the drum and rotated by the drum through multiple cycles of heating the photopolymerizable layer, contacting the layer with a web of an absorbent material, separating the absorbent material from the layer, and cooling the layer. It took 3 thermal cycles to completely remove the release layer in the exposed plate surfaces. Processed plates were light finished and post-exposed same time for 10 minutes each. The relief depth and the depth of the reverse line of a 31.5 mil negative line (reverse depth) were measured for each Comparative and reported below.

The remaining exposed plate, Control 1, was solvent washed in an imine CYREL 1001P solvent processor with OPTISOL solvent. It was dried in 60° C. oven for 1.5 hours, and then light finished and post-exposed the same time for 10 minutes each. Control 1 had a relief depth of 41 mils. The measurement of the reverse line (31.5 mils negative line) showed a reverse depth of 600 micron.

The plate used for Example 1 was a CYREL photopolymer plate, type DPH (67 mils). The composition of the

24

photopolymerizable layer of the DPH plate was the same as the photopolymerizable layer for the HOS that was used for the Comparatives and Control samples. The DPH plate included the photopolymerizable layer, an infrared-sensitive, a laser ablatable (i.e., actinic radiation opaque) layer, and a coversheet. The actinic radiation opaque layer included 67 wt. % of Macromelt® 6900 polyamide as a binder and 33 wt. % of carbon black. The Macromelt polyamide binder has a softening point of 135° C.

The sample plate for Example 1 was backflushed for 12 seconds on the Kelleigh exposure unit. After discarding the coversheet, the plate was mounted on the drum of the CYREL Digital Imager with the actinic radiation opaque layer facing out, and the plate was held tight with vacuum on the drum and with tapes on all sides. Artwork images equivalent to the silver halide targets as described for the Comparatives and Control were laser ablated onto the radiation opaque layer using Nd:YAG laser (light wavelength output at 1064 nm). Excellent *in situ* mask on plate was obtained with the laser ablation energy of 3.2 Jules/cm<sup>2</sup>. The actinic radiation opaque layer of Example 1 had the visual transmission density of 2.95, and the ablated solid had a stain density of 0.10 (transmission). The ablated plate was given a main UV exposure in the open air (under atmospheric oxygen) for 9 minutes on the CYREL 2001 exposure unit.

The resulting plate was thermally treated using the same thermal processor and the same processing conditions as described above for the Comparative Examples 1A and 1B except that the plate of Example 1 was thermally treated for 6 thermal cycles of heating and contacting with the absorbent material. The UV exposed black mask images were completely removed after first thermal cycle. Surprisingly, even though the infrared-sensitive layer contains carbon black, an unmeltable compound, the remaining portions of the layer were completely removed during thermal development. The plate was light finished and post-exposed for 10 minutes at the same time.

The relief depth and the reverse depth for Example 1 was measured and reported below.

Example	Relief Depth (mil)	Reverse Depth (micron)
Comparative 1A	22	231
Comparative 1B	33	260
Control 1	41	600
Example 1	21.8	380

Example 1 showed a dramatic improvement in reverse depth with equivalent relief depth when compared to Comparative 1A. It was surprising that given the same thermal processing conditions, the exposure conditions of laser ablation to form the mask and exposure in open air of Example 1 provided such a dramatic improvement over that of the analog exposed Comparative 1A with a silver halide target under the vacuum pull.

The reverse depth (for a 31.5 mil negative line) of Example 1 was much deeper than the reverse depth of Comparative 1A and 1B processed for 6 or 12 thermal cycles. However, the thermally treated plates of Example 1 and Comparatives 1A and 1B gave lower relief depth and lower reverse depth than that of solvent processed plate of Control 1, even though all samples were given the same backflash and main UV exposure levels.

The plates of Example 1, Comparative 1A and 1B and the Control were printed on a Mark Andy Press System 830

## US 6,773,859 B2

25

(Chesterfield, Mo.). Film III Dense Black EC8630 ink (Environment Inks & Coatings, Morgantown, N.C.) was diluted with EIC Aqua Refresh EC1296 (with a mixture of two solvents) to give a viscosity of 27 seconds as measured using a Zahn #2 cup. Printing was done on Hi-Gloss 40FS S246 paper (Fasson, Painsville, Ohio), at 100 feet/minute.

The plate of Example 1 which was UV exposed in atmospheric air through the mask had excellent print quality of the whole tonal scale, excellent print of slur targets and excellent solid printing. It was surprising and unexpected to find that the thermal treated plates of Comparative 1A and 1B gave significantly poorer printing performances than that of the solvent treated plate, Control 1. Dirty printing of dots from mid-tone to shadow areas (40-99%), dirty slur target printing, and patchy (uneven) solid printing were observed for the Comparatives 1A and 1B while the Control 1 gave good and sharp printing results for both the tonal range scale and slur targets. This showed that the processing method has dramatic effect on how the unexposed areas are being removed effectively between the dots and fine reverses as well as how the exposed release layer is being removed from the exposed plate surface, and thus on the final printing performance difference. Thermal processing is much less effective in removing the unexposed photopolymer areas and the exposed release layer on the plate surface than the solvent processing (with a mixture of two solvents) under the brush, and thus much poor printing quality.

It was unexpected to find that the plate of Example 1 (exposed thru in situ mask in the open air with no additional layers on the plate sample) had dramatically improved printing performance when compared to the plate of Comparative 1A (analog exposure through target film under vacuum with Kreen coversheet on top). This was particularly surprising since the plate of both Example 1 and Comparative 1A were thermally treated for 6 cycles and given the same levels of backflash and imaging exposures. It was also very surprising to find that the 70% nominal dots (60.4% measured) of Example 1 gave much cleaner printing than that of 50% nominal dots of Comparative 1A (52.7% measured). This showed that UV exposure conditions play an extremely important role for plates that are thermally processed to form the relief.

## Example 2

The following example demonstrates process of this invention using photosensitive elements each having a thermally removable layer and one or more additional layers above the photopolymerizable layer.

For Controls A and B, each top layer was coated from a 4% solid solution on a temporary substrate (Mylar® polyester 5 mils thick) to form a continuous coating with minimum of surfactant present as the coating aid. After the coating was allowed to dry (at least overnight for room dried coatings), the temporary substrate with the dried coating was hot laminated to a photopolymerizable layer. For all samples except Example 2A and 2C, the photopolymerizable layer was from a CYREL photopolymer printing plate, type UXL, 67 mils thick. The coversheet and release layer were removed prior to lamination for all samples in which the photopolymerizable layer originated from CYREL printing plate. The coating and temporary substrate was laminated such that the top layer was disposed above the surface of the photopolymerizable layer opposite the support.

For Example 2A, a plate structure was assembled as follows. A CYREL photopolymer plate, type AQS, (67 mils) having the release layer removed was used as the photopolymerizable layer. A second element having multiple layers including a radiation opaque layer was laminated to the photopolymerizable layer of the AQS plate. The second

26

element was prepared and included in the following order an adhesion modifying layer of 90 parts Macromelt 6900 polyamide and 10 parts copolymer of vinylpyrrolidone and vinyl acetate (60/40 ratio) (PVP-VA-630) having a coating weight of 3.0 mg/dm<sup>2</sup>; a radiation opaque layer of 16.9 grams of BS-11548 carbon black pigmented dispersion (from CDI Dispersions) (see Ex. 8) and 2.80 grams of Polyox WSRN polyethylene oxide, the layer having a density of 3.0; and an overcoat layer of 100% solution of Polyox WSRN polyethylene oxide having a coating weight of 40 mg/dm<sup>2</sup>, on a temporary MYLAR polyester support. The plate structure was the temporary MYLAR support as a coversheet, the adhesion modifying layer, the radiation opaque layer, the overcoat layer as a barrier layer, and the AQS photopolymerizable layer on a permanent support.

For Example 2B, a separate element was prepared by coating onto a temporary support a radiation opaque layer of 33 wt. % carbon black and 67% Macromelt polyamide (dried coating weight of 26 mg/dm<sup>2</sup>), and then a layer of polyethylene wax (coating weight of 8 mg/dm<sup>2</sup>). The separate element was laminated to the UXL photopolymerizable layer such that the photosensitive element had the following structure, a coversheet of the temporary support, the radiation opaque layer, the wax layer, UXL photopolymerizable layer on a permanent support.

For Example 2C, a plate structure was assembled as follows. A CYREL photopolymer plate, type HCS, (67 mils) having the release layer removed was used as the photopolymerizable layer. A second element was prepared by coating onto a temporary support a radiation opaque layer of 33 wt. % carbon black and 67% Macromelt polyamide (dried coating weight of 15 mg/dm<sup>2</sup>); and then a layer of a copolymer of vinylpyrrolidone and vinyl acetate, (PVP-VA-W735 from International Specialty products), (20 mg/dm<sup>2</sup> coating weight). The second element was laminated to the HCS photopolymerizable layer such that the photosensitive element had the following structure, a coversheet of the temporary support, the radiation opaque layer, the PVP-VA layer, HCS photopolymerizable layer on a permanent support.

40

Name	Description	Softening Point (or Other)
Macromelt ® 6900	Polyamide from Henkel Corporation, Polymer Division	135° C.
PVP-VA W735	Copolymer of vinylpyrrolidone and vinyl acetate from International Specialty Products	141° C.
PVP-VA-630	Copolymer of vinylpyrrolidone and vinyl acetate (60 and 40 ratio) from International Specialty Products	Not available
Polyox WSRN-750	Polyethylene oxide from Union Carbide	65° C. (melt point) <100° C. (melt pt.)
Polyethylene wax		

Each element was backflash exposed for 15 seconds on the CYREL 2001 exposure unit. The temporary coversheet was removed. Half of each element was given an overall exposure of 9 minutes to ultraviolet radiation through the thermally removable layer side on the exposure unit in the open air, while the other half of the element was covered with a film which blocked UV light. (There was no image-wise exposure of the element.) This allowed one to observe the thermal processability of the element both in the unex-

## US 6,773,859 B2

27

posed state and UV exposed state. Elements were thermally processed in a CYREL Fast 1000 TD processor at the processing conditions below.

The cycles required to remove the thermally removable layer were noted and a maximum of 12 thermal cycles of heating and contacting was given for each element. The relief depth after 12 thermal cycles was measured. The elements were assessed for the performance of the material as a thermally removable layer. A satisfactory thermally removable layer on the thermally processed element, is one in which the thermally removable layer is removed with minimal thermal cycles from at least the unexposed areas of the underlying photopolymer layer, and also allows effective removal of the unexposed photopolymer layer. In some cases, it is necessary for the thermally removable layer in the exposed areas of the photopolymerizable layer to also be removed during thermal treatment. (Minimal thermal cycles are preferably less than 12 cycles of heating and contacting the element with an absorbant material.) If there is residual material from the top layer on the exposed photopolymer surface, the residual material should not interfere with the ultimate printing performance of the plate and thus should provide good and even printing surfaces.

The processing conditions for the thermal were set as follows:

Developer roll temperature:	275° F.
Drum temperature:	95° F.
Pressure:	2.2 psi/inch
Plate speed:	30 inches/minute
IR setting:	80% of maximum
Relief setting:	20 mils
Blower:	automatic

All elements were given first a heating cycle and followed by heating and contacting cycles up to 12 cycles of heating and contacting with an absorbent web, CEREX® non-woven nylon.

Table 1 lists the material used for the thermally removable (T.R.) layer, the total coating weight of the layers on the photopolymerizable layer including the thermally removable layer/s, the number of thermal cycles required to remove the exposed and unexposed T.R. layer, the relief depth of the photopolymer layer after 12 cycles of heating and contacting with the absorbent material, and the overall assessment of the thermally removable layer in thermal processing.

28

The results of Example 2 show that the thermally removable layer as well as multiple additional layers on the photopolymerizable layer can be removed by thermal processing. Further, the top layer can be thermally removed even when the top layer contains carbon black, a material that is non-meltable, with a binder which is softenable or meltable at the thermal treating temperature. The melting or softening point of the binder material forming one or more additional layers on the photopolymerizable material should be less than the temperature for thermal treating the element. While it is preferred to have the lower melting or softening temperature of the binder in the thermally removable layer and the one or more additional layers, the melting or softening temperature is not the only factor to be considered. For instance, compatibility or incompatibility of the binder material in the thermally removable layer or the one or more additional layers with the migratory materials (e.g., monomer and photoinitiator) in the photopolymerizable layer when adjacent the photopolymerizable must be considered. If the binder in the layer adjacent the photopolymerizable layer is compatible with the migratory materials in the photopolymerizable layer, the thermal processability of the top layer may be detrimentally affected.

## Example 3

25 The following example demonstrates the process of this invention in which the physical form of the organic binder used in the thermally removable layer has an important effect on thermal processability of a photopolymer plate.

30 Similar to Example 2, each top layer for the Comparative Examples was coated from a 4% solid solution on a temporary substrate (Mylar® polyester 5 mils thick) to form a continuous coating with minimum of surfactant present as the coating aid. After the coating was allowed to dry (at least 35 overnight for room dried coatings), the temporary substrate with the dried coating was hot laminated to a photopolymerizable layer. For all samples in this Example, the photopolymerizable layer was from a CYREL photopolymer printing plate, type UXL, 67 mils thick, in which the coversheet and release layer were removed prior to lamination. The coating with the temporary substrate was laminated to the photopolymerizable layer such that the top layer was disposed above the surface of the photopolymerizable layer opposite the support.

40 45 For Examples A and 3B, each of the Elvanol compounds were separately applied as a powder onto the tacky photopolymerizable surface of a UX plate (having release layer removed). Elvanol 75-15, a fully hydrolyzed (99%) polyvi-

TABLE 1

Example	Material for T.R. Layer	Ctg. Wt. (mg/dm <sup>2</sup> )	Cycles needed to remove T.R. layer		Cycles needed to remove T.R. layer		Relief (mils)	Assess- Unexp. ment
			Exposed	Unexposed	Exposed	Unexposed		
Control A	Macromelt 6900	42	1	1	1	1	19.5	Excellent
Control B	PVP-VA-630	11.8	2	1	1	1	21.2	Good
2A	Multilayer: T.R.L. of polyethylene oxide and carbon black	58	1	1	1	1	32	Excellent
2B	Multilayer: T.R.L. of polyamide and carbon black	34	1	1	1	1	25.5	Excellent
2C	Multilayer: T.R.L. of polyamide and carbon black	35	1	1	1	1	good relief	Excellent

## US 6,773,859 B2

## 29

nyl alcohol, and Elvanol 50-42, a 88% hydrolyzed polyvinyl alcohol (12% vinyl acetate), were supplied by the vendor, DuPont, in powder form.

Name	Description	Softening Point (or Other)
Elvanol 75-15	Fully hydrolyzed (99%) polyvinyl alcohol from DuPont Co.	Not softenable, degrades at 200° C.
Elvanol 50-42	88% hydrolyzed polyvinyl alcohol (12% vinyl acetate) from DuPont Co.	Not softenable, degrades at 200° C.
Klucel G	Hydroxypropyl cellulose from Aqualon (molecular wt. 370,000)	130° C.
Klucel E	Hydroxypropyl cellulose from Aqualon (molecular wt. 80,000)	100° C.

The release layer of a 67 UXL plate was removed with tape to provide the photopolymerizable layer with a tacky surface, and Elvanol 75-15 was applied as a powder by pad toning for 20 cycles, creating plate sample Example 3A. Loose powders were wiped off from the plate surface with a LasStik cloth. A second UXL plate was similarly toned with Elvanol 50-42 powder, creating plate sample Example 3B. In both cases, the toned UXL plate surface became tack-free, which showed that Elvanol powders were indeed on the plate surface as desired. Both plates were given a backflash exposure of 15 seconds on CYREL 2001 exposure unit.

The resulting two plates, Examples A and 3B, were thermally treated on the CYREL Fast 1000 TD machine under the same conditions as described in Example 2. It was surprising to find that both polyvinyl alcohol compounds in powder form were completely removed from the unexposed photopolymer plate surfaces after one cycle of heating (the plate) and contacting (the plate surface) with the absorbent material. The relief depths for both plates of Example 3A and 3B were 26 mils after 12 cycles of heating and contacting with absorbent material.

## 30

element including the removal of the unexposed photopolymerizable areas. However, the results of Examples 3A and 3B showed that when organic binder is used in the powder form (or as particulates), on the surface of the photopolymerizable layer, the softening or melting point of the binder is no longer a limitation for thermal removal of the layer formed of particulates together with the underlying unexposed photopolymerizable areas. Comparative Examples 3C and 3D each had a continuous film coating of a hydroxypropyl cellulose material as the top layer on the photopolymerizable layer.

The use of hydroxypropyl cellulose as a release layer on a photopolymerizable layer was disclosed by Wang in EP 0 665 471 A2 (see Examples 3, 4, Comp. 3, and Comp. 4). The top layer coating of Comparative Example 3C was not usable because the exposed areas of the top layer remained on the polymerized plate surface as uneven strings and those strings gave poor printing results. The top layer coating of Comparative Example 3D gave fair results because the exposed areas required longer thermal cycles to remove the top layer. The results are fairly consistent with those shown by Wang. Softening/melting point of a material forming a continuous coating on the photopolymerizable layer plays a role in thermal processability. Lower softening temperature is preferred for thermal processing of plates.

Other high softening or melting organic powders were also applied to the tacky surface of the photopolymerizable layer of a UXL plate and tested following the same test method as described above in this Example for polyvinyl alcohol powders. The materials used were cellulose acetate powder (melt point of 230° C.) and cellulose acetate butyrate (melt point of 155° C.) (both from Eastman Kodak). Only one thermal cycle of heating and contacting absorbent material was required to remove the unexposed powder and good relief depth of 27 mils was obtained after 12 cycles of heating and contacting absorbent layer.

Results showed that the physical form of the organic binder used in the thermally removable layer has an important effect on thermal processability of the photosensitive element.

Ex.	Material for T.R. Layer	Ctg. Wt. (mg/dm <sup>2</sup> )	Cycles needed to remove T.R. layer Exposed	Cycles needed to remove T.R. layer Unexposed	Relief (mils)	Assess- Unexp. ment
Comp 3A	Elvanol 75-15 (film form ctg.)	11.76	>>12 not removable	>>12 not removed	zero	Not good
Comp 3B	Elvanol 50-42 (film form ctg.)	11.44	>>12 not removable	>>12 not removed	zero	Not good
Comp 3C	Klucel G (film form ctg.)	21.89	>>2 not removable	Removed in 1 cycle but as strings	21	Not good
Comp 3D	Klucel E (film form ctg.)	6.64	7	1	29	Fair
3A	Elvanol 75-15 (powder)	—	1	1	26	Excellent
3B	Elvanol 50-42 (powder)	—	1	1	26	Excellent

Surprisingly, the results of Examples 3A and 3B are completely different from that observed in Comparative Examples 3A and 3B where no relief depth was obtained for Elvanol 75-15 and Elvanol 50-52 as a continuous film on the same photopolymer plate even in the unexposed areas. Both Elvanol 75-15 and Elvanol 50-42 are not softenable and degrade at about 200° C. When used as a binder in a continuous film-forming layer as in Comparative Examples 3A and 3B, the melting or softening point of the binder in a top layer can influence the thermal developability of the

## Example 4

The following example demonstrates the process of this invention in which a layer of particulate material is the thermally removable layer on the photopolymerizable layer. The particulate material forms a radiation opaque layer.

Similar to Example 3, a CYREL photopolymer plate, type UXL (67 mil) was prepared (i.e., release layer and cover-sheet removed) for application of different black powder materials. Carbon black is a non-meltable compound. The

## US 6,773,859 B2

## 31

black particulate material was applied to achieve black transmission density of at least 2.00 (visual filter). Loose powders were wiped off with Lastic cloth. In Example 4A, Cromalin® black toner KK6-CN (available from DuPont Co.) which comprises carbon black and cellulose acetate (melt point 230° C.) was used and the density of the toned layer on the plate was 2.98. In Example 4B, a black electrostatic toner (from Lanier) which comprises carbon black and styrene acrylate polymer was used and the density of the toned layer on the plate was 2.63. The particle size measurement was conducted on a Coulter® Multisizer instrument. Particle size was reported as equivalent spherical diameter in microns and the volume distributions at 10%, 50%, and 90% (in microns) are as follows for each of the toners.

Material	d10	d50	d90
KK6-CN	4.29	7.51	18.20
Electrostatic Toner	6.91	10.72	15.38

For Example 4C, a different CYREL photopolymer plate, type EXL, (67 mil) was prepared similar to Example 3 and toned with the KK6-CN powder. Type EXL plate includes on the photopolymerizable layer an elastomeric capping layer which has a blue color. The density of the black toner layer was 2.08.

All plates of Examples 4A–4C, were given a backflash exposure of 15 seconds on CYREL 2001 Exposure unit and then overall exposed to UV radiation through the black particulates side in the open air (in the presence of atmosphere oxygen) for 9 minutes. That is, no imagewise exposure was given to the element. This overall exposure simulated the exposure conditions experienced by opaque areas of an in situ mask on an element having an infrared sensitive layer. Thus the UV exposed black particulates that can form an in situ mask must also be thermally removable, together with the underneath photopolymer layer to give desired relief depth.

All plates of Examples 4A–4C were thermally treated in the CYREL Fast 1000TD thermal processor under the same processing conditions as described in Example 2. Surprisingly, only one cycle of heating (the plate) and contacting the absorbent (to the outermost surface of the plate) was required to remove the layer of black particulates for Example 4B with the underlying photopolymer layer. Only two cycles were needed to remove the layer of black particulates for Examples 4A and 4C with the underlying UXL and EXL photopolymer layers respectively. Good deep relief depth was obtained for all three plates after 12 cycles of heating and contacting the absorbent material.

Example	Relief Depth (mils)
4A	35 mils
4B	26 mils
4C	27 mils

The results demonstrated that excellent thermal removal of radiation opaque particulates on photopolymer plate surface with the underlying (unpolymerized) photopolymer layer and in situ UV mask property can be achieved as desired.

## 32

## Example 4D

For Example 4D, another UXL plate with the KK6-CN black particulate as described above in Example 4 was prepared similar to Example 4A, but density of the black toner layer was 2.24 on the plate. The plate of Example 4D was given the backflash exposure of 20 seconds in the Kelleigh Exposure unit, and then placed on a drum of the CYREL Digital Imager as described in Example 1. The black particulate layer was laser ablated at 2.4 Joules/cm<sup>2</sup> using the same images as in Example 1. Excellent ablated images were obtained and the ablated solid had a stain density of 0.08 transmission density. The laser ablation step formed an in situ mask on the photopolymerizable layer. The laser-ablated plate was then UV exposed through the in situ mask side in the open air for 10 minutes on the Kelleigh Exposure unit. The plate was thermally processed in the CYREL Fast 1000TD with the same processing conditions as in Example 2. Only two cycles of heating and contacting with absorbent material were needed to remove the black particulate layer with the underlying photopolymer layer. The relief depth after 12 cycles of heating and contacting the absorbent material was 23 mils. There were no residual black toner particulates on the floor nor in the fine reverses of the relief imaged plate. After post-exposure and finishing, the plate was used for printing on a Mark Andy press with conditions and materials as described in Example 1. The plate of Example 4D gave excellent processed images and excellent print quality for the whole tonal range, slur targets and solid as desired.

## Example 5

The following example demonstrates the process of this invention in which layer of inorganic particulates is the thermally removable layer on the photopolymerizable layer. The inorganic particulates have a melting point well above the thermal treating temperature used to melt, soften or remove the unpolymerized areas of the photopolymerizable layer.

Similar to Examples 3 and 4, a layer of a particulate material was applied by toning to the tacky surface of a photopolymerizable layer of a CYREL photopolymer plate, type UXL (67 mils) having the release layer removed. For Example 5A, aluminum silicate (sold as Satin White from Englehard) (melt point 1000° C.) was used. The particle size measurement was conducted on a Coulter® Multisizer instrument. Particle size was reported as equivalent spherical diameter in microns and the volume distributions at 10%, 50%, and 90% (in microns) are as follows.

	d10	d50	d90
Satin White	3.16	6.73	13.67

The excess powder was wiped off with LasStik cloth. The surface of the plate having the particulate layer was tack-free.

The plate of Example 5A was given backflash exposure of 15 seconds on CYREL 2001 exposure unit. The plate was thermally treated on the CYREL Fast 1000 TD machine under the same processing conditions as in Example 2. Surprisingly, only one thermal cycle was required to remove the (unexposed) particulates of Example 5A from the plate surface. For Example 5A, the relief depth was 20 mils after 12 cycles of heating and contacting with absorbent material.

Similar good results were also obtained for particulate material of titanium dioxide (melt point of 1560° C.) toned

## US 6,773,859 B2

## 33

on the photopolymerizable layer. The toned particulate material provided the element with a tack-free surface and was removed in the first thermal cycle during thermal treating.

## Example 6

The following Example demonstrates the importance of the size of particulates forming a thermally removable layer on the photopolymerizable layer in the process of this invention. The thermally removable layer is formed of metal and metal alloy particulates having a high melting point. By proper selection of particle size, the metallic particulates can be used to form in situ mask and be removed thermally with the unpolymerized areas of the photopolymerizable layer.

Similar to Examples 3 and 4, a layer of a particulate material was applied by toning to the tacky surface of a photopolymerizable layer of a CYREL photopolymer plate, type UXL (67 mils) at room temperature. To ensure good coverage of these particulates for in situ mask application, plates were toned twice (40 toning cycles each time). Loose particulates were wipe off with LasStik cloth.

For Example 6A, the particulate layer was formed of MS-1, aluminum flakes (melt point 660° C.) having less than 5% stearic acid (obtained from Alcan Toyo America). The reported average particle size (By Microtrac) was 32 micron. For Examples 6B and 6C, the particulate layer was formed of XB-260 Pale and Resist CT Pale metal alloys (obtained from Eckart America L. P.), respectively. According to Material Safety Data Sheets supplied by Eckart, XB-260 Pale comprises of 85–95% copper, 5–15% zinc, and 0.2–2.0% stearic acid, with a reported average particle size of 5 micron (Cilas method), and, Resist CT Pale comprises 68–88% copper, 9–29% zinc and 3% SiO<sub>2</sub> with a reported average particle size of 35 um (Cilas method). The particle size of the particulate was also measured in our lab. Particle size measurement was conducted on a Coulter® Multisizer instrument. Particle size was reported as equivalent spherical diameter in microns and the volume distribution results (in microns) are as follows.

Particulate	D10	d50	d90
MS-1	12.8	27.14	41.05
XB-260	2.46	3.95	21.63
Resist CT Pale	7.88	18.32	24.63

The d50 is the median wherein half of the sample's mass consists of particles smaller than the given diameter in microns. The d90 means that 90% of the sample's mass consists of particles smaller than the given diameter in microns. For particulate to be used as a radiation opaque mask, the volume distributions at d50 and d90 should be considered.

The transmission density (with visual filter) of Examples 6A, 6B, and 6C on the plate was 1.15, 2.07 and 1.02, respectively. All toned plate surfaces were tack-free. It was surprising that the particulates of Example 6B (XB-260) which had the smallest average particle size among three metallic particulates, provided the highest transmission density under the same toning conditions.

All plates of Examples 6A–6C were given a backflash exposure of 20 seconds in the Kelleigh exposure unit. The plates were laser ablated to imagewise remove the particulate layer on the CYREL Digital Imager with a Nd:YAG laser emitted at about 1064 nm with the same image file as

## 34

in Example 1, and form a mask. All three plates had good ablated images. The optimum laser ablation energy was determined to be 5.9, 3.2 and 5.9 Joules/cm<sup>2</sup> for Example 6A, 6B, and 6C respectively. The ablated solid area had a transmission density of 0.07, 0.37 and 0.16 for Example 6A, 6B, and 6C, respectively. Big metallic particles were observed on the ablated surface of the photopolymerizable layer for plates of Example 6A and 6C. Gray residue was observed on the ablated surface of the photopolymerizable layer for the plates of Example 6B. All the plates that had been ablated were UV exposed in the open air through the metal and metal alloy (mask) side for 9 minutes on CYREL 2001 exposure unit.

All plates were then thermally processed on the same thermal processor and with the same conditions as described in Example 2 for 12 cycles of heating and contacting with the absorbent material.

After 12 cycles of heating and contacting with the absorbent material, the plate of Example 6C had extremely low relief depth (2.5 mils) and there were lots of the metallic particulates remaining in the floor and in the fine reverses (more than on the ablated area surface). Also there were residual particles on top of the surface of the plate of Example 6C to the extent that the transmission density in these areas was 0.10. Similar results were obtained for the plate of Example 6A. Surprisingly, the plate of Example 6B had good relief of 17 mils after 12 cycles of heating and contacting absorbent and all the particulates were removed with the underlying photopolymerizable layer in 2 cycles of heating and contacting with the absorbent material. The floor areas and the fine reverses were free of the metallic particulates. After post-exposure and light finishing for 10 minutes (which was conducted at the same time), all the plates were printed on Mark Andy press as described in Example 1. Very good printed images were obtained for the plate of Example 6B but poor printing was encountered for plates of Example 6A and 6C. Poor printing was the result of the low floor relief of the processed plate. Due to the size of the particles for the particulate material of Examples 6A and 6C were

Comparative Examples to the invention demonstrated in Example 6B. It is believed that satisfactory results can be obtained with the particulate material of Comparative Examples 6A and 6C if the particulate material would be ground to the desired size, i.e., less than 23 microns.

Low relief depth of (Comparative) Examples 6A and 6C could be explained by the fact that these plates had low density (low UV blocking capability), and photopolymerization of the underneath photopolymerizable areas took place during UV exposure through the particulates. In order to provide a functional UV in situ mask, the toned metallic particulates must have transmission density greater than 2.0. A higher toned density of particulates represents a higher degree of packing of the particles on the plate surface. This was better achieved with particulates having smaller particle size volume distribution at d50 and d90 as was demonstrated in this Example. Smaller particulate size of the thermally removable layer was also useful in the thermal processing step. The smaller particles were more easily removed from the fine reverses and between dot areas of the plate surface. The particulate having large size tended to remain on the plate surface and in the fine reverses after thermal processing, and detrimentally affected printing performance.

This example also demonstrated the unexpected advantage of single processing step (thermal treatment only) is possible with a photopolymerizable element having a layer of metallic particulate. No additional aqueous potassium hydroxide solution was required to remove the metallic

## US 6,773,859 B2

35

mask (by vacuum deposition) before the solvent developer step to remove the uncrosslinked diazo layer as described in the Example 1 of U.S. Pat. No. 4,132,168. This also gives improved overall turnaround time.

## Example 7

The following example demonstrates an element and the process of this invention in which a coating of an inorganic dispersion of a filler agent and a binder form the thermally removable layer on the photopolymerizable layer.

Two stock solutions were made. Elvanol® 50-42, a 88% hydrolyzed polyvinylalcohol (12% vinyl acetate), was dissolved in distilled water to give 4% solution. Ludox® AM, a 30% solid of colloidal silica (from DuPont Co.) was diluted with distilled water to give 4% solution. The average particle diameter of colloidal silica is 12 nanometers. A very small amount of Silwet surfactant was added to both solutions. Dried silica has a melting point of 1900° C. The dried particles of colloidal silica are chemically inert and heat resistant.

Two composite solutions were made from the 4% stock solutions and each was coated on 5 mil Mylar® polyester film with 2 mil doctor knife. The final dried coating compositions were 70% silica/30% Elvanol 50-42 by weight for Example 7A and 85% silica/15% Elvanol 50-42 for Example 7B. Each of the coatings for Examples 7A and 7B was a composite coating since the organic binder is in the discontinuous phase (that is the binder is less than 49% by weight of the total composition). For Example 7C, a third coating of only the silica stock solution was also made under the same conditions.

The coatings were dried at least for overnight room temperature and then were each coating was hot laminated to the photopolymerizable layer of a CYREL photopolymer plate, type UXL, (67 mil). The release layer of the plate was removed prior to lamination of the coating. Each sample was backflushed for 15 seconds in the CYREL 2001 exposure unit. The temporary MYLAR sheet was removed from the samples. Correct adhesion balance was obtained for all samples and the coatings adhered to the tacky photopolymer surface to give tack-free surface as desired.

The samples of Examples 7A-7C were thermally processed in the same thermal processor under the same conditions as described in Example 2.

Surprisingly, for Example 7 B and Example 7C only one thermal cycle of heating and contacting with an absorbant material was necessary for the coating (i.e., thermally removable layer) to be removed with the unexposed photopolymerizable layer. For Example 7A, the coating was removed with the unexposed photopolymerizable layer in two thermal cycles. The relief depth after 12 cycles of

36

heating and contacting with the absorbent material was 17 mils for Example 7A, 29 mils for Example 7B and 20 mils for Example 7C.

Comparatively, the continuous film made from Elvanol 50-42 (also from 4% solid solution and 2 mil knife coating) could not be used as the thermally removable layer for a photopolymer plate when thermally processed as described and shown in Example 3 (Comparative Example 3B). No relief depth was obtained in the unexposed areas of the plate even after 12 cycles of heating and contacting absorbent material.

This Example showed that it is possible to use as the thermally removable layer an extremely high melting inorganic material, e.g., silica having a melting point of 1900° C., as a filler, as well as an organic binder having a high melting point, such as polyvinyl alcohol which degrades at 200° C., to form a composite layer on the photopolymerizable layer, and yet, the photosensitive element will thermally process suitably. This demonstrated that softening and/or melting point limitations are not applicable to a photosensitive element having a thermally removable layer with less than 49 wt. % binder.

## Example 8

The following example demonstrates the element and the process of this invention in which the thermally removable layer (b) is an actinic radiation opaque layer. The radiation opaque layer is based on carbon black dispersions or mixtures of carbon black dispersion and organic binder. Such coatings, after application to the photopolymer plate surface, can be digitally imaged and thermal processed.

Several coating solutions were prepared. BS11548 & BS15870 are carbon black pigmented aqueous dispersions from CDI Dispersions. BS 11548 dispersion has a total % solid of 51% that comprises 45% pigment and 6% of proprietary material. BS 15870 dispersion has a 46% total solid that comprises 38% pigment and 8% proprietary material. Each dispersion was diluted to 4% solution with distilled water, and small amount of surfactant (Zonyl FSN) was added. The diluted solutions were coated onto 5 mil Mylar® temporary supports with 2 mil doctor knife. The transmission density of the resulting dry coatings was 3.7 and 3.1 for BS 11548 (Coating A) and BS 15870 (Coating B), respectively.

Four more coating solutions were prepared by mixing the 4% Elvanol 50-42 (a 88% hydrolyzed polyvinyl alcohol (12% vinyl acetate)) stock solution (from Example 7) and the 4% BS 11548 dispersion so that the dried compositions were as follows. (Elvanol 50-42 is not softenable and degrades at 200° C.) Each of the dispersions was coated on 5 mil MYLAR polyester film using a 2 mil doctor knife, forming Coatings C, D, E, and G.

Coating	Weight % Carbon Black	Weight % Elvanol 50-42	Weight % Other proprietary material	Transmission Density (visual filter)	% binder per total binder + carbon black filler)
A	88.2	—	11.8	3.7	0
B	82.8	—	17.2	3.1	0
C	49	44	7	2.8	47.3
D	70.3	20.5	9.2	3.4	22.8
E	83.8	5	11.2	3.1	5.6
G	25	71.7	3.3	3.6	74.1

## US 6,773,859 B2

37

Another coating solution was prepared from a mixture of the 4% BS 11548 dispersion and the 4% aqueous solution of Klucel G, hydroxypropyl cellulose from Aqualon, with a small amount of surfactant (Zonyl FSN). (The melting point of Klucel G is 130° C.) This coating solution was coated with a 2 mil doctor knife onto 5 mil MYLAR polyester film. The resulting Coating F had a composition of 83.8% carbon black, 5% hydroxypropyl cellulose, and 11.2% proprietary material, and the transmission density measured was 2.5.

Another coating solution was prepared from a mixture of Alcotex 552P, a colloidal dispersion in water of a copolymer of vinyl alcohol and vinyl acetate (55/45) (from Harco, having an estimated melting point of 150 to 180° C.) and the carbon black dispersion and coated with a doctor knife onto polyester film to have a dried coating weight of 17 mg/dm<sup>2</sup>. The resulting Coating H had a composition of 49% carbon black, 44% copolymer of vinyl alcohol and vinyl acetate, and 7% proprietary material (from dispersion), and the transmission density measured was 2.85.

Coating	Weight % Carbon Black	Weight % Binder	Weight % Other proprietary material	Transmission Density (visual filter)	% binder per total binder + carbon black filler)
F	83.8	5	11.2	2.5	5.6
H	49	44	7	2.85	47.3

All Coatings A-H were each hot laminated to a CYREL photopolymer plate, type UXL, (67 mil), such that the Coating layer was on the photopolymerizable layer of the plate, forming plate samples for Examples 8A, 8B, 8C, 8D, 8E, 8F, and 8H, and Comparative Example 8G. The release layer of the plate had been removed prior to lamination. In all Examples 8A-8F, 8H, and Comparative 8G, the coating layer became a radiation opaque layer. Each plate sample was backflash exposed of 15 seconds on the CYREL 2001 exposure unit. The MYLAR sheet (support for the Coating) was removed from each plate sample. Correct adhesion balance of the coating to the photopolymerizable layer was observed for Examples 8C, 8D, 8E, 8F, and 8H, and Comparative 8G. The Coatings A and B had somewhat higher adhesion to MYLAR (temporary support) such that care was taken while removing the MYLAR so that the coating layer remained on the photopolymerizable layer. All plate samples were given an UV exposure through the radiation opaque (coating) layer for 9 minutes in the open air on Cyrel® 2001 Exposure unit.

All plate samples were thermally processed in the same thermal processor and with the same processing conditions as described in Example 2. A cycle or thermal cycle is the heating of the plate sample and contacting of the surface of the plate with an absorbent material. All radiation opaque coatings gave the desired thermal processing properties and good actinic radiation mask as desired for Examples 8A-8F and 8H.

Example	Number of Cycles to Remove Radiation Opaque Layer	Relief Depth After 12 Cycles (mils)
8A	2	26
8B	2	30
8C	6	17

38

-continued

Example	Number of Cycles to Remove Radiation Opaque Layer	Relief Depth After 12 Cycles (mils)
8D	4	25
8E	2	24
8F	2	19
8H	1	23
Comp. 8G	>12	0.3

However, for the plate of Comparative Example 8G greater than 12 cycles of heating and contacting was required to remove the radiation opaque layer from the element. Also even though the transmission density of the coating layer was sufficiently high (3.6) and thus provided good blocking to the UV radiation, the plate had low relief depth. The coating layer of Comparative Example 8G was not thermally removable and prevented the removal of the underlying unexposed photopolymerizable material. The

coating G had greater than 49% binder (based on the total of binder and filler), and thus was not a discontinuous layer.

Further comparatively, the continuous coating layer of Elvanol 50-42 (88% hydrolyzed polyvinyl alcohol) on the photopolymerizable layer could not be thermally processed even in the unexposed area (no relief depth) as described above in Example 3 (Comparative Example 3B). The continuous coating layer of Klucel G (hydroxypropyl cellulose) on the photopolymerizable layer could not be thermally removed in the UV exposed area due to string formation after 12 cycles of heating and contacting absorbent material as described in Example 3 (Comparative Example 3C).

## Example 9

The following example demonstrates the element and process of this invention in which the thermally removable layer is a radiation opaque layer that is on the photopolymerizable layer.

Example 8 was repeated except that the coating solutions were made from different materials. A binder solution of copolymer of vinylpyrrolidone and vinyl acetate in a 60/40 ratio (PVP-VA-630 from International Specialty Products) was dissolved as a 4% aqueous solution with small amount of surfactant (Zonyl FSN) added. The binder solution was mixed with the 4% BS 11548 carbon black dispersion of Example 8, such that the dried composition was 49% carbon black, 44% binder and 7% of proprietary material (47.3 wt % binder based on total of binder and carbon black filler), and coated on MYLAR polyester film. The coating had a dry transmission density of 2.5. The coating was then laminated to the photopolymerizable layer of a photopolymer plate (type UXL) as described in Example 8. The plate samples were backflushed, the MYLAR film removed, and then UV exposed through the black layer as described in Example 8.

The plate samples were thermally processed in the same thermal processor and under the same conditions as described in Example 2. For the plate samples, only one

## US 6,773,859 B2

39

thermal cycle was needed to remove the radiation opaque layer together with the underneath polymer layer. The relief depths were 23–26 mils after 12 cycles of heating and contacting absorbent material. Each plate sample met the desired properties as the digital plate capable of being thermally processed.

## Example 10

The following example demonstrates the process of this invention in which the thermally removable layer is an actinic radiation opaque mask that can be delivered by conventional ink jet methods or as a physical mask screen onto the photopolymerizable layer.

This inkjet-mask concept was simulated by writing images on the surface of a CYREL photopolymer plate, type UXL, with and without the presence of the release layer on the photopolymer layer, using a black Sharpie permanent Marker (multiple writing to achieve desired density) as the actinic radiation mask. The resulting plates were UV imaged through the ink mask side in the presence of atmospheric oxygen for 9 minutes on a CYREL 2001 exposure unit, backflushed for 15 seconds on the exposure unit, and then thermally processed using the thermal processor and processing conditions as in Example 1. The masks of black ink were thermally removed after first thermal cycle and gave good processed image and relief as desired.

The physical mask was simulated by attaching black vinyl letters (with pressure sensitive adhesive) (from Visu-Com Inc.) on the surface of a CYREL photopolymer plate, type UXL (67 mil), with and without the presence of the release layer on the photopolymer layer, prior to main UV exposure. Exposure to UV radiation through the physical masks (letters) in open air and backflash exposure was carried out as described above for the inkjet mask. After removing the physical mask letters, the plate was processed thermally to give excellent letter images with good relief after 12 cycles of heating and contacting absorbent material as desired.

It is expected that other methods of forming the actinic radiation mask on the photopolymerizable layer would provide just as good of results as above using the thermal process. Mask images could be done by laser ablation transfer mechanism through another donor mask film, or laminating a mask images on a temporary support and then discarding the temporary support.

## Example 11

The following example demonstrates the process of this invention for digital mask exposures in which the photo-sensitive element includes one or more layers with the thermally removable layer and the photopolymerizable layer.

The following general procedure was conducted after the product structures as described below were assembled. The plate was backflushed for 20 seconds on a Kelliegh exposure unit. The temporary coversheet discarded and the plate was placed on a CYREL Digital Imager so that the radiation opaque layer (black coating) was facing the laser. The plate was imagewise exposed to laser radiation that ablated the radiation opaque layer from the plate. The image file at the laser energy level as described in Example 1 was used for the imagewise laser exposure. The plate was UV exposed in the Kelliegh exposure unit for 10 minutes in the presence of atmospheric oxygen. The plate was thermally processed in the same thermal 1000TD processor with the same processing conditions as described in Example 2. Post exposure and light finishing were carried out before printing the plate on the Mark Andy press as described in Example 1.

40

For Example 11A, a plate structure was assembled as follows. A CYREL photopolymer plate, type HOS (67 mils) and a LaserMask® digital imaging film (from Rexam) having a radiation opaque (black) layer of an optical density of 2.8 were laminated together. The plate structure was a temporary MYLAR coversheet, LaserMask™ opaque layer, a release layer of Macromelt 6900 polyamide (coating weight of 24 mg/dm<sup>2</sup>), and the HOS photopolymerizable layer on permanent support. The photopolymerizable layer included a binder, at least one monomer and a photoinitiator. The ablated solid has a density of 0.06 after being laser ablated at energy of 1.6 Joules/cm<sup>2</sup>. Thermal processing showed that only one thermal cycle was required to remove the opaque layer and the release layer with the underlying photopolymer layer, and the relief depth after 12 cycles of heating and contacting absorbent was 23 mils. Excellent print quality was also obtained on Mark Andy press for the postexposed and finished plate.

For Example 11B, a plate structure was assembled as follows. A CYREL photopolymer plate, type AQS, (67 mils) having the release layer removed was used as the photopolymerizable layer. A second element having multiple layers including a radiation opaque layer was laminated to the photopolymerizable layer of the AQS plate. The second element was prepared and included in the following order an adhesion modifying layer of 90 parts Macromelt 6900 polyamide and 10 parts copolymer of vinylpyrrolidone and vinyl acetate (60/40 ratio) (PVP-VA-630) having a coating weight of 3.0 mg/dm<sup>2</sup>; a radiation opaque layer of 16.9 grams of BS-11548 carbon black pigmented dispersion (from CDI Dispersions) (see Ex. 8) and 2.80 grams of Polyox WSRN polyethylene oxide, the layer having a density of 3.0; and an overcoat layer of 100% solution of Polyox WSRN polyethylene oxide having a coating weight of 40 mg/dm<sup>2</sup>, on a temporary MYLAR polyester support. The plate structure was the temporary MYLAR support as a coversheet, the adhesion modifying layer, the radiation opaque layer, the overcoat layer as a barrier layer, and the AQS photopolymerizable layer on a permanent support. The ablated solid areas of the plate had a density of 0.05 using 3.2 J/cm<sup>2</sup> laser energy. Only one thermal cycle was required to remove the radiation opaque layer and the relief depth was 32 mils after 12 cycles of heating and contacting with the absorbent material.

For Example 11C, a plate structure was assembled as follows. A CYREL photopolymer plate, type UXL (67 mils), and a second element having a radiation opaque layer were laminated together. The second element was prepared and included the radiation opaque layer of 33% carbon black and 67% Kraton 1102 an elastomeric poly(styrene-butadiene-styrene) block copolymer having a density of 2.60, and a barrier layer of 100% polyamide having a coating weight of 42 mg/dm<sup>2</sup>, on a temporary MYLAR support with silicon treated surface. The plate structure was the temporary MYLAR support as a coversheet with the silicon treated surface adjacent the radiation opaque layer, the barrier layer, and the UXL photopolymerizable layer on a permanent support. The ablated solid area on the plate had a density of 0.12 with laser ablation energy of 3.2 J/cm<sup>2</sup>. Four thermal cycles were required to remove the exposed radiation opaque layer completely with the underneath photopolymerizable layer. The relief depth of 22 mils was obtained after 12 cycles of heating and contacting with the absorbent material. Good printed images were obtained.

## Example 12

The following example demonstrates the process of this invention with excellent thermal processing latitude.

## US 6,773,859 B2

41

Three CYREL photopolymer plates, type DPH, (45 mil) were backflushed for 75 seconds on Kelleigh exposure unit. The DPH plate has the following structure: a permanent blue support; the DPH photopolymerizable layer comprising an elastomeric binder, at least one monomer, and a photoinitiator; a radiation opaque layer of 33% carbon black and 67% Macromelt polyamide, and a coversheet. After discarding the coversheet, the plate was placed on the drum of the CYREL Digital Imager and laser ablated at 3.2 J/cm<sup>2</sup> to form in situ mask images as described in Example 1. The plates were exposed to UV radiation through the in situ mask for 14 minutes in the presence of atmospheric oxygen.

The plates were thermally treated in the same thermal processor as described in Example 1. One plate (A) was processed for 12 cycles with blower on, another plate (B) was processed for 12 cycles with blower off, and the third one (C) was processed for 6 cycles with blower off. All plates were light finished and post-exposed for 10 minutes simultaneously. The relief depth and reverse depth for a 30 mil negative line of the processed plates were measured, and the plates were printed. The base (i.e., the permanent support) temperature of the plate as it was treated in the thermal processor was also measured. The results were as follows:

Plate	Number of Cycles	Relief Depth (mil)	Reverse Depth (micron)	Base Temp. ° C.	Printing
A	12	24	265	77	Excellent
B	12	24	255	82	Excellent
C	6	17	268	77	Excellent

The excellent processing latitude of digitally exposed, but thermally processed plates has been demonstrated. This Example also showed that the number of thermal cycles could be reduced significantly (from 12 down to 6 cycles) and still providing excellent print quality in holding all tonal ranges and fine reverses, and good clean solid printing. Reduced number of cycles will provide a faster turnaround time for the plate.

## Example 13

The following example demonstrates the process of this invention in which particle size and volume distribution of particulate material forming a substantially transparent layer on a photosensitive element, influences the thermal processing performance of the element.

A photopolymerizable layer was from a CYREL photopolymer printing plate, type UXL, 67 mils thick, in which a coversheet and a release layer were removed prior to toning. Particulate material was toned on the tacky UXL photopolymer surface by following the same procedures as in Example 3. The photosensitive element comprised support, the UXL photopolymerizable layer, and a layer of particulate material.

The particulate materials that were toned were two types of aluminum silicate powder (Satin White and Sparker, both from Englehard). Satin White has a reported particle size range of 4 to 35 microns and Sparker has a reported particle size range of 10 to 110 microns by the light scattering method according to Englehard. Particle size analysis according to our lab testing on the Coulter® Multisizer as in Example 6, showed particulate size and volume distribution as follows, in microns.

42

	d10	d50	d90
Satin White	3.16	6.73	13.67
Sparker	11.65	30.26	47.7

The excess particulate was removed from the photopolymer surface, and the toned density was measured as a transmission density using a visual filter. Both toned surfaces were tack-free indicating particulate adhering to the plate surface as desired. Example 13A was the element formed of UXL photopolymerizable layer toned with Satin White particulate. Example 13B was the element formed of UXL photopolymerizable layer toned with Sparker particulate. The visual density was 0.39 for Example 13A and 0.14 for Example 13B. The higher visual density of Example 13A relative to Example 13B showed that higher packing system was achieved with the Satin white powder vs. Sparker powder on toned plate surface.

Half of each sample element was given an UV exposure in the presence of atmospheric oxygen and the other half was not UV exposed. Samples were processed thermally as in Example 3.

It was surprising to find that the toned particulate layer of Example 13A was removed in the first thermal cycle in both exposed and the non-exposed areas. For Example 13A, the relief depth was 20 mils after 12 cycles in the non-exposed areas with no residual particulate on the floor. Also, the UV exposed plate surface was tacky and with no sign of residual particulate. In comparison, for Example 13B, there was still particulate on the floor surface even after 12 thermal cycles with 22 mil relief depth in the non-exposed areas, and the UV exposed plate surface was tack-free due to the presence of particulates on the surface.

Both samples were post exposed and light finished and were printed on Mark Andy press as in Example 1. Example 13A gave good solid printing while Example 13B gave poor solid printing (much lower solid density). Residual aluminum silicate particles on the thermally processed plate surface and floor were not desirable. Residual particles on the floor indicated hard-to-remove nature of Sparker (higher d50 and d90 in micron) and this problem could be worsen for images with high screen ruling images and with fine reverses to cause poor thermal cleaning of plate, thus poor print quality.

The above results showed that particle size and distribution have important impact on the particle packing relationship, and optical effect, thus final thermally processed plate performance. The particle size and volume distribution of Satin White provides the preferred range for thermally processed plate.

## Example 14

The following example demonstrates the process of this invention using a photosensitive element having a radiation opaque layer that includes a binder with a softening point less than 190° C.

A CYREL photopolymer plate, type UXL, (67 mils) was used as the photopolymerizable layer. The release layer was removed. A second element was prepared with a radiation opaque layer of 17% carbon black and 83% Macromelt polyamide (melting point 135° C.), having a dried coating weight of 47 mg/dm<sup>2</sup> and a transmission density of 2.50. The radiation opaque layer was laminated to the UXL photopolymerizable layer, forming sample element for Example 14.

## US 6,773,859 B2

43

The radiation opaque layer was imagewise ablated from the photopolymerizable layer forming a mask with infrared laser radiation having energy of 5.9 Joules/cm<sup>2</sup>. The ablated solid density was 0.19. The element was given a backflash exposure for 20 seconds, and a main UV exposure through the mask for 10 minutes, both on the Kelleigh exposure unit. The element was thermally processed as described in Example 2. Only one cycle (of heating and contacting the element) was required to remove the remaining portions of the radiation opaque layer. The relief depth after 12 cycles was 26 mils. The element was prepared for printing as described above, and had good print results.

What is claimed is:

1. A process for making a flexographic printing plate comprising:
  - 1) providing a photosensitive element comprising: at least one photopolymerizable layer on a support comprising an elastomeric binder, at least one monomer, and a photoinitiator, and at least one thermally removable layer disposed above the photopolymerizable layer, the thermally removable layer selected from the group consisting of
    - (a) an actinic radiation opaque layer comprising (i) at least one infrared absorbing material, (ii) a radiation opaque material, wherein (i) and (ii) can be the same or different, and at least one binder having a softening or melting temperature less than 190° C.;
    - (b) a layer of a composition comprising at least one binder and filler, wherein the binder is less than 49% by weight based on the total weight of the binder and filler, and
    - (c) a layer of particulate material having particle size of less than 23 micrometers;
  - 2) imagewise exposing the photopolymerizable layer to actinic radiation forming polymerized portions and unpolymerized portions; and
  - 3) thermally treating the element of step 2) by heating to a temperature sufficient to remove the thermally removable layer and to remove the unpolymerized portions of the photopolymerizable layer and form a relief.
2. The process of claim 1 wherein the thermally removable layer selected from b) and c) is a release layer.
3. The process of claim 1 wherein the thermally removable layer selected from b) and c) is an actinic radiation opaque layer.
4. The process of claim 3 wherein the thermally removable layer b) further comprises (i) at least one infrared absorbing material, (ii) a radiation opaque material, wherein (i) and (ii) can be the same or different.
5. The process of claim 3 wherein the thermally removable layer c) is radiation opaque and the particulate material can be a radiation opaque material, both a radiation opaque and infrared absorbing material, or combinations thereof.
6. The process of claim 1 wherein the thermally removable layer completely covers the photopolymerizable layer.
7. The process of claim 3 wherein the thermally removable layer is a mask layer having radiation opaque areas, further comprising the step of forming the mask layer imagewise from the thermally removable layer selected from a), b), or c), prior to step 2).
8. The process of claim 7 wherein forming the mask comprises applying the thermally removable layer imagewise to the photopolymerizable layer.
9. The process of claim 7 wherein forming the mask comprises applying as a complete covering layer the thermally removable layer to the photopolymerizable layer, and imagewise removing the thermally removable layer.

44

10. The process of claim 7 wherein forming the mask comprises forming a carrier element having the thermally removable layer as the imagewise mask on a temporary support, laminating the carrier element to the photopolymerizable layer such that the thermally removable layer is disposed above a surface of the photopolymerizable layer opposite the support, and removing the temporary support.

11. The process of claim 7 wherein forming the mask comprises delivering imagewise the thermally removable layer by ink jet methods.

12. The process of claim 7 wherein the thermally removable layer is also sensitive to infrared radiation and forming the mask comprises:

15 forming a carrier element having the thermally removable layer on a substrate;  
 placing the carrier element onto the photopolymerizable layer such that the thermally removable layer is disposed above a surface of the photopolymerizable layer opposite the support;  
 imagewise exposing with infrared radiation the thermally removable layer to selectively change the adhesion balance of the thermally removable layer to substrate of the carrier element; and  
 removing the substrate with portions of the thermally removable layer.

13. The process of claim 7 wherein the thermally removable layer is also sensitive to infrared radiation and forming the mask comprises:

30 placing a first element comprising at least the thermally removable layer on a substrate so that the thermally removable layer is in contact with or disposed above a surface of the photopolymerizable layer opposite the support;  
 imagewise exposing with infrared laser radiation the thermally removable layer to selectively transfer portions of the thermally removable layer to the photopolymerizable layer; and  
 separating the first element with portions of the thermally removable layer.

14. The process of claim 7 wherein the thermally removable layer is also sensitive to infrared radiation and forming the mask comprises:

35 imagewise exposing with infrared laser radiation the thermally removable layer to selectively ablate portions of the thermally removable layer from the photopolymerizable layer.

15. The process of claims 12, 13, and 14 wherein the infrared laser radiation is between 760 to 1064 nm.

16. The process of claims 12, 13, and 14 further comprising impinging the infrared laser radiation on the thermally removable layer or through the support side of the photosensitive element.

17. The process of claim 16 wherein the infrared laser radiation impinges the support side of the photosensitive element and further comprising locating a material capture element adjacent to the photosensitive element on a side opposite the support side to capture ablated portions of the thermally removable layer.

18. The process of claim 3 wherein the imagewise exposing step 2) occurs in the presence of atmospheric oxygen.

19. The process of claim 3 wherein the photosensitive element further comprises an additional layer between the thermally removable layer and the photopolymerizable layer, the additional layer being thermally removable at the treating temperature, and composed of materials selected from the group consisting of: polyamide, polyethylene

## US 6,773,859 B2

45

oxide, polypropylene oxide, polyethylene wax, natural waxes, synthetic waxes, polypropylene, polyethylene, copolymers of styrene and acrylic polymers, copolymers of vinylpyrrolidone and vinyl acetate, copolymers of vinyl alcohol and vinyl acetate, polyacetate, copolymers of ethylene and acetate, and combinations thereof.

20. The process of claim 1 wherein the photosensitive element further comprises a adhesion-modifying layer on the thermally removable layer, the adhesion-modifying layer being thermally removable at the treating temperature, and composed of materials selected from the group consisting of: polyamide, natural waxes, synthetic waxes, polyprylene, polyethylene, copolymers of polyvinylpyrrolidone and vinyl acetate, amphoteric interpolymers, and combinations thereof.

21. The process of claim 1 wherein the photosensitive element further comprises at least one more additional layer selected from the group consisting of:

release layer, adhesion-modifying layer, barrier layer, and surface modifying layer, wherein the at least one more additional layer is transparent to actinic radiation.

22. The process of claim 1 wherein the binder of the thermally removable layer (a) is selected from the group consisting of: polyamides, polyethylene oxide, polypropylene oxide, ethylcellulose, hydroxyethyl cellulose, cellulose acetate butyrate, ethylene-propylene-diene terpolymers, copolymers of ethylene and vinyl acetate, copolymers of vinyl acetate and vinyl alcohol, copolymers of vinyl acetate and pyrrolidone, polyvinyl acetate, polyethylene wax, polyacetal, polybutyral, polyalkylene, polycarbonates, polyester elastomers, cyclic rubber, copolymers of styrene and maleic anhydride, copolymers of styrene and maleic anhydride partially esterified with alcohols, and combinations thereof.

23. The process of claim 1 wherein the binder of the thermally removable layer (b) is selected from the group consisting of: polyamides, polyethylene oxide, polypropylene oxide, ethylcellulose, hydroxyethyl cellulose, cellulose acetate butyrate, ethylene-propylene-diene terpolymers, copolymers of ethylene and vinyl acetate, copolymers of vinyl acetate and vinyl alcohol, copolymers of vinyl acetate and pyrrolidone, polyvinyl acetate, polyethylene wax, polyacetal, polybutyral, polyalkylene, polycarbonates, polyester elastomer, copolymers of vinyl chloride and vinyl acetate, copolymers of styrene and butadiene, copolymers of styrene and isoprene, thermoplastic block copolymers of styrene and butadiene, thermoplastic block copolymers of styrene and isoprene, polyisobutylene, polybutadiene, polychloroprene, butyl rubber, nitrile rubber, thermoplastic polyurethane elastomer, cyclic rubbers, copolymers of vinylacetate and (acrylate or methacrylate), acrylonitrile-butadiene-styrene terpolymer, methacrylate-butadiene-styrene terpolymer, alkyl methacrylate polymer or copolymer, copolymers of styrene and maleic anhydride, copolymers of styrene and maleic anhydride partially esterified with alcohols, polyvinyl alcohol, poly(meth)acrylic acids, metal alkali salts of poly(meth)acrylic acids, amphoteric interpolymers, hydroxyalkyl cellulose, cellulose acetate, nitrocellulose, polyimides, polyesters, polyphenylene ethers, polyacrylonitril, polystyrene, copolymers of styrene and methacrylic acid, polyvinyl chloride, polyesters, polyacrylamide, copolymers of imides and amides, polychlorotrifluoroethylene, ethylene and chlorotrifluoroethylene copolymer, polytetra fluoroethylene, copolymers of ethylene and tetrafluoroethylene copolymer, polyether ether ketone, polybenzimidazoles, copolymers of vinylidene fluoride and hexafluoropropylene, and combinations thereof.

46

24. The process of claim 1 wherein the filler is selected from the group consisting of: mineral fillers, metallic fillers, metallic alloys, flame retardants, carbon black, graphite, pigments, and combinations thereof.

25. The process of claim 24 wherein the filler has a particle size of less than 23 micrometers.

26. The process of claim 1 wherein the particulate material is selected from the group consisting of: metals, metal alloys, carbon black, graphite, organic particles, inorganic particles, pigment particles, toner particles, mixtures of pigment particles, mixtures of toner particles, and mixtures of pigment and toner particles, and combinations thereof.

27. The process of claim 1 wherein the at least one infrared absorbing material (i), the radiation opaque material (ii), the filler, and the particulate material in the thermally removable layer do not melt at the treating temperature.

28. The process of claim 1 wherein the total amount of the at least one infrared absorbing material (i) and the radiation opaque material (ii) in the thermally removable layer (a) is less than 49% by weight, based on the total weight of (i), (ii) and the binder of (a).

29. The process of claim 1 wherein the thermally removable layer (b) is capable of microcracking to allow unexposed portions of the photopolymerizable layer to melt, soften, or flow at the treating temperature.

30. The process of claim 1 wherein the thermally removable layer is (a).

31. The process of claim 1 wherein the thermally removable layer is (b).

32. The process of claim 1 wherein the thermally removable layer is (c).

33. The process of claim 1 wherein the binder of the thermally removable layers (a) and (b) has a softening or melting temperature between 100° C. and 190° C.

34. The process of claim 33 wherein the binder of the thermally removable layer (b) has a softening or melting temperature greater than 190° C.

35. The process of claim 1 wherein the binder of the thermally removable layer (a) is greater than 51% by weight, based on the total weight of (i), (ii) and the binder.

36. The process of claim 1 further comprising contacting the photosensitive element of step 2) with an absorbent material during the treating step 3).

37. The process of claim 36 further comprising applying pressure of 0.70 kilograms per square centimeter to about 7.03 kilograms per square centimeter during contacting the element and the absorbant material.

38. The process of claim 36 further comprising applying pressure of 2.11 kilograms per square centimeter and about 4.92 kilograms per square centimeter during contacting the element and the absorbant material.

39. The process of claim 1 wherein the thermal treating is heating the photosensitive element above about 40° C.

40. The process of claim 39 wherein the thermal treating is heating the photosensitive element to between 100 and 200° C.

41. The process of claim 36 wherein the heating of the photosensitive element and the contacting of the element with the absorbant material defines a cycle, and wherein the treating step comprises more than one cycle.

42. The process of claim 41 wherein for each cycle the treating temperature and the pressure independently can be the same or different.

43. The process of claim 2 wherein imagewise exposing further comprises:

placing a phototool imaged film on the thermally removable layer,

## US 6,773,859 B2

47

exposing through the phototool with actinic radiation to selectively image the photopolymerizable layer, and removing the phototool prior to the step 3).

44. The process of claim 2 wherein imagewise exposing further comprises:

placing at least one template having radiation opaque portion on the thermally removable layer,  
exposing through the template with actinic radiation to selectively image the photopolymerizable layer, and removing the at least one template prior to step 3).

45. The process of claim 3 further comprising ablating the actinic radiation opaque layer from the photopolymerizable layer, to form an in situ mask on the photopolymerizable layer prior to the imagewise exposing step 2).

46. The process of claim 1 wherein at least 90 percent of the particulate (c) have the particle size of an equivalent spherical diameter of less than 23 micrometers.

47. The process of claim 1 wherein at least 50 percent of the particulate (c) have the particle size of an equivalent spherical diameter of less than 17 micrometers.

48. The process of claim 1 wherein the thermally removable layer is present prior to the imagewise exposing step 2).

49. The process of claim 3 wherein the thermally removable layer is radiation opaque and is present during the imagewise exposing step.

50. The process of claim 1 wherein the at least one thermally removable layer is less than 50 microns thick.

51. A photosensitive element for use as a flexographic printing plate comprising:

at least one photopolymerizable layer on a support comprising an elastomeric binder, at least one monomer and a photoinitiator, wherein the photopolymerizable layer in an unexposed state is capable of melting, softening, or flowing at a treating temperature of at least 40° C., and

at least one thermally removable layer disposed above the photopolymerizable layer, wherein the thermally removable layer comprises at least one binder and a filler, wherein the binder is less than 49% by weight based on the total weight of the binder and filler.

48

52. The photosensitive element of claim 51 wherein the thermally removable layer has a thickness less than 50 microns.

53. The photosensitive element of claim 51 wherein the thermally removable is an actinic radiation opaque layer.

54. The photosensitive element of claim 51 wherein the binder of the thermally removable layer is selected from the group consisting of: polyamides, polyethylene oxide, polypropylene oxide, ethylcellulose, hydroxyethyl cellulose, cellulose acetate butyrate, ethylene-propylene-diene terpolymers, copolymers of ethylene and vinyl acetate, copolymers of vinyl acetate and vinyl alcohol, copolymers of vinyl acetate and pyrrolidone, polyvinyl acetate, polyethylene wax, polyacetal, polybutyral, polyalkylene, polycarbonates, polyester elastomer, copolymers of vinyl chloride and vinyl acetate, copolymers of styrene and butadiene, copolymers of styrene and isoprene, thermoplastic block copolymers of styrene and butadiene, thermoplastic block copolymers of styrene and isoprene, polyisobutylene, polybutadiene, polycholorprene, butyl rubber, nitrile rubber, thermoplastic polyurethane elastomer, cyclic rubbers, copolymers of vinylacetate and (acrylate or methacrylate), acrylonitrile-butadiene-styrene terpolymer, methacrylate-butadiene-styrene terpolymer, alkyl methacrylate polymer or copolymer, copolymers of styrene and maleic anhydride, copolymers of styrene and maleic anhydride partially esterified with alcohols, polyvinyl alcohol, poly(meth)acrylic acids, metal alkali salts of poly(meth) acrylic acids, amphoteric interpolymers, hydroxyalkyl cellulose, cellulose acetate, nitrocellulose, polyimides, polyesters, polyphenylene ethers, polyacrylonitril, polystyrene, copolymers of styrene and methacrylic acid, polyvinyl chloride, polyesters, polyacrylamide, copolymers of imides and amides, polychlorotrifluoroethylene, ethylene and chlorotrifluoroethylene copolymer, polytetra fluoroethylene, copolymers of ethylene and tetrafluoroethylene copolymer, polyether ether ketone, polybenzimidazoles, copolymers of vinylidene fluoride and hexafluoropropylene, and combinations thereof.

\* \* \* \* \*

UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : 6,773,859 B2  
DATED : August 10, 2004  
INVENTOR(S) : Fan Roxy et al.

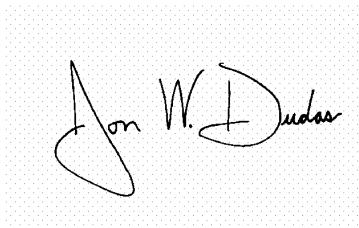
Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 45,  
Line 13, "polyprpylene" should read -- polypropylene --

Signed and Sealed this

First Day of March, 2005



JON W. DUDAS  
*Director of the United States Patent and Trademark Office*

UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : 6,773,859 B2  
DATED : August 10, 2004  
INVENTOR(S) : Fan et al.

Page 1 of 1

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

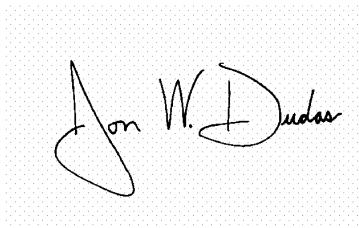
Title page,

Insert Item -- [60] **Related U.S. Application Data**

Provisional application No. 60/273,669, filed on March 6, 2001 --

Signed and Sealed this

Twenty-sixth Day of July, 2005

A circular, dotted background containing a handwritten signature in black ink. The signature reads "Jon W. Dudas".

JON W. DUDAS  
*Director of the United States Patent and Trademark Office*

**CERTIFICATE OF SERVICE**

I hereby certify that copies of the foregoing NONCONFIDENTIAL BRIEF OF PLAINTIFF-APPELLANT were served upon registered counsel by operation of the Court's CM/ECF system on this 18<sup>th</sup> day of September, 2015.

<b>John Richard Horvack, Jr.</b> <b>Fatima Lahnin</b> CARMODY TORRANCE SANDAK & HENNESSEY LLP 195 Church Street 18 <sup>th</sup> Floor New Haven, CT 06509-1950  <i>Attorneys for Appellee</i>	<p>[ <input type="checkbox"/> ] By United States Mail [ <input type="checkbox"/> ] By Legal Messenger <b>[X] By Electronic CM/ECF</b> [ <input type="checkbox"/> ] By Overnight Express Mail [ <input type="checkbox"/> ] By Facsimile <b>[X] By Email [courtesy copy]</b> jhorvack@carmodylaw.com flahnin@carmodylaw.com</p>
--	---

Dated: September 18, 2015

Respectfully submitted,

/s/ Donna Stockton

Donna Stockton

**CERTIFICATE OF COMPLIANCE**

I certify that the foregoing BRIEF OF PLAINTIFF-APPELLANT contains 13,173 words as measured by the word processing software used to prepare this brief.

Dated: September 18, 2015

Respectfully submitted,

*/s/ Howard W. Levine*

Howard W. Levine  
Finnegan, Henderson, Farabow,  
Garrett & Dunner, LLP  
901 New York Avenue, NW  
Washington, DC 20001  
(202) 408-4000

*Attorney for Plaintiff-Appellant*